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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIV NOVEMBER 1959 No. 11

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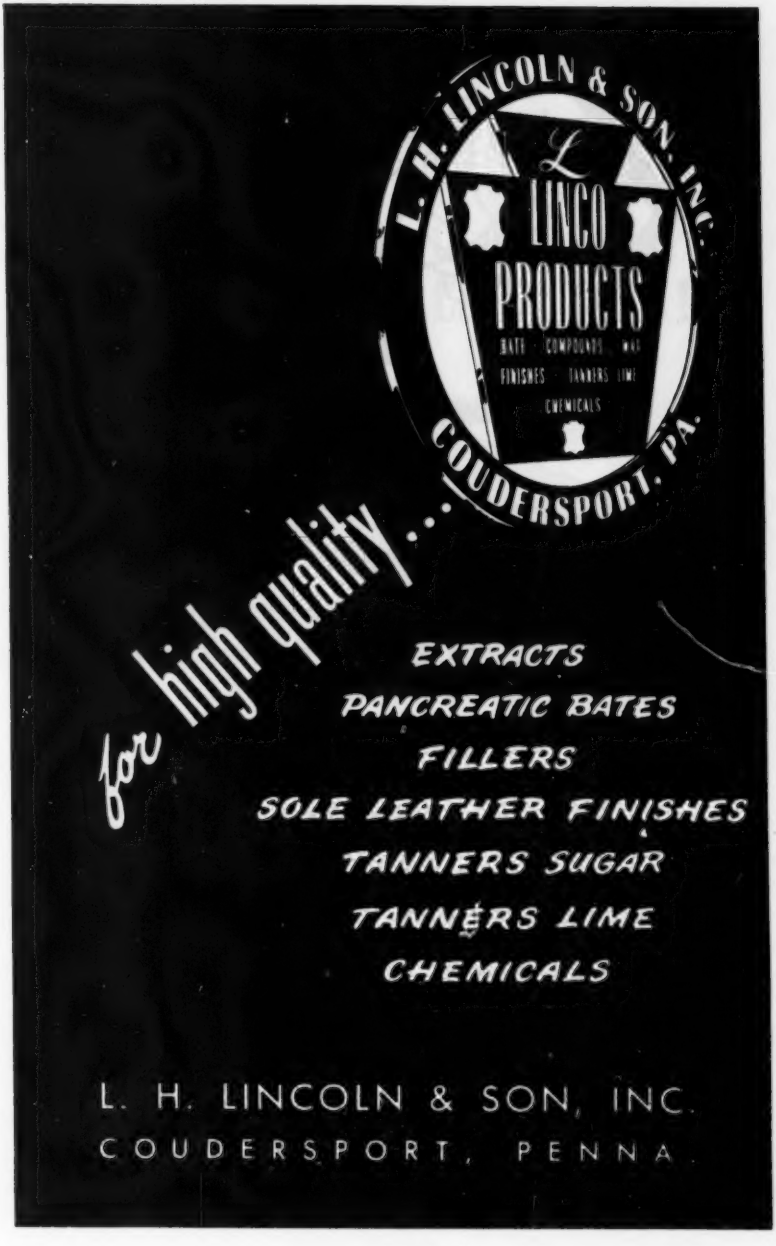
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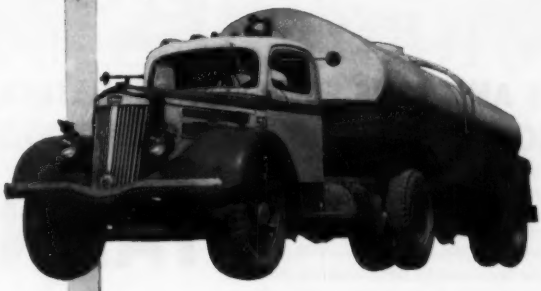

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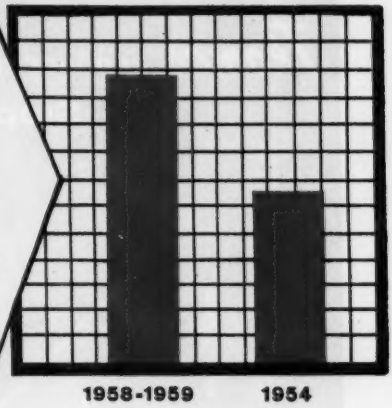

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SOME RECENT ADVANCES IN THE CHEMISTRY AND BIOCHEMISTRY OF COMMERCIALLY IMPORTANT CONDENSED TANNINS*

D. G. Roux

Leather Industries Research Institute, Rhodes University, Grahamstown, South Africa

ABSTRACT

Progress in the chemistry of condensed tannins may be assessed by placing emphasis mainly on those compounds which have been isolated and characterized in detail, or which appear to be precursors in the path of biogenesis of tannins.

The tannins of wattle and quebracho extract consist of a mixture of components representing an even molecular-weight gradation over the ranges M = 550–3250 and 800–2350 respectively. From black wattle extract (−) 7, 3′, 4′, 5′-tetrahydroxyflavan-3-ol ((−)-robinetinidol), first of the resorcinol series of naturally occurring catechins, (+)-catechin and (+)-gallocatechin have been identified, and the distribution of these catechins in related wattles has also been established. (−)-Robinetinidol appears to be a characteristic component of black wattle and closely related barks. The catechin and leucoanthocyanin chemistry of the extracts places emphasis on the "flavonoid" nature of complex wattle tannins present.

The detailed chemistry of (−) 7, 3′, 4′-trihydroxyflavan-3, 4-diol ((−)-leucofisetinidin), shown to be a prototype of quebracho tannins, is described. The biosynthesis of tannins from this constituent in quebracho heartwood is described, and the reason for its absence in the commercial extract is established. The relative importance of this compound in relation to quebracho tannins is determined from the yields of fisetinidin produced from each.

Support for the concept of flavan-3, 4-diols as basic units of condensed tannins is obtained also from mangrove bark extract and from other sources, and possible mode of linkage of flavan-3, 4-diols to other or similar "flavonoid" nuclei in tannin formation is discussed.

*Paper read at the Sixth Congress of the International Union of Leather Chemists Societies in Munich, Germany, on September 7, 1959.

The importance of recent advances of condensed tannin chemistry in relation to some aspects of leather chemistry, e.g., redness of vegetable extracts, their reaction with bisulfite, identification of condensed tannins in leather, and the tannin-collagen affinity relationship, is reviewed.

—✕—✕—

INTRODUCTION

As with most natural products, progress in the chemistry of the condensed tannins is limited by difficulties experienced in resolving by means of existing methods the exceptionally complex mixtures of phenolic compounds present in almost all commercial vegetable tanning extracts. Recent work by Roux and Evelyn (1, 2) has shown that the typical condensed tannins of wattle and quebracho extracts consist of an even gradation over the ranges 550–3250 and 800–2350 respectively of interrelated components (1, 3) in which no single substance predominates. Such uniform distribution, the apparent structural similarity, the high degree of hydroxylation, and the relatively high molecular weight of the major fraction of the components, all contribute toward their mutual association during partition or adsorption separation procedures and consequently militate against their isolation in sufficient yield for accurate identification.

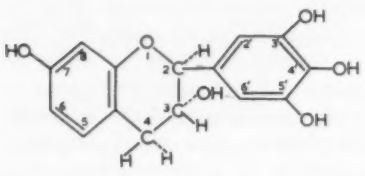
While these difficulties bear due recognition, it has recently been shown that Craig countercurrent partition separations (4) and adsorption and partition separations on cellulose (5, 6, 7) are effective for isolating at least some of the "flavonoid" components of wattle and quebracho extracts. At this stage it is also possible to predict that many more components will be isolated by means of these methods.

Against this background it should be recognized that the alternative method of "identification" of new components by paper chromatographic evidence alone must be regarded as speculative, and that even for known compounds the classical procedure of isolation and characterization has no substitute. Only where for some reason components cannot be isolated, and where evidence of their identity is supported by a combination of (*a*) similar RF values in different and selective solvent systems, (*b*) similar color reactions with selective chromogenic reagents, (*c*) a similar shift in the ultraviolet absorption spectra on complexing with metal ions or under alkaline conditions, and (*d*) similar infrared adsorption spectra, all in comparison with reference compounds, is the paper chromatographic method valid [see methods of Nordstrom and Swain (8, 9) and Geissman, Jorgenson, and Harborne (10)].

The earlier isolation of the minor components of wattle and quebracho tannins has already been reviewed (11). In this paper the more recent chemistry of some of the major or significant components of wattle, quebracho, mangrove, and some other extracts is described and related to tanning theory and to certain aspects of the tanning process.

THE CATECHINS AND LEUCOANTHOCYANINS OF BLACK WATTLE BARK EXTRACT

Black wattle tannins from the fresh bark of *Acacia mollissima* have been shown by Roux and Maihs (6, 12) to contain a mixture of catechins from which they isolated (−) 7, 3′, 4′, 5′-tetrahydroxyflavan-3-ol (I), (+)-catechin (II) and (+)-gallocatechin (III) by means of adsorption and partition chromatography on cellulose. I was obtained simultaneously by



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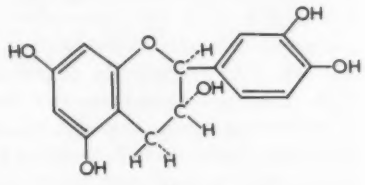

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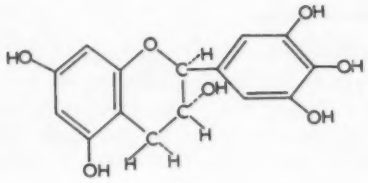
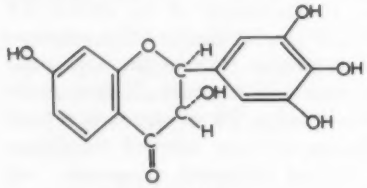


III

synthetic means by Weinges (13) through the catalytic reduction of (+) 2, 3-dihydrorobinetin (IV) to (+) 7, 3′, 4′, 5′-tetrahydroxyflavan-3, 4-diol (V) using the method of Freudenberg and Roux (14), followed by the catalytic hydrogenolysis of the latter at the 4-position to (−)-robinetinidol (I).



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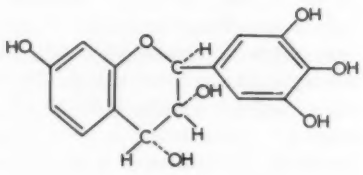
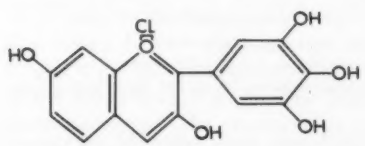


V

Comparison of the derivatives of the synthetic and natural products established their identity (6, 12). This catechin is the first of the resorcinol series to be isolated from natural sources. Previously it was considered by Roux (15) to be a possible prototype of black wattle tannins, and by analogy to the previous work of Freudenberg and Maitland (16), has been termed "black wattle catechin" (6). Weinges (13) related the absolute configuration of these compounds (I, IV, V) of the resorcinol series to that of (+)-catechin, and I therefore has a 2,3-*trans* configuration of substituent groups in the heterocyclic ring.

Roux (17) previously (1953) tentatively identified (+)-catechin and (+)-gallocatechin by means of paper chromatography, and in unpublished work King (18) (1957) isolated (+)-catechin from commercial wattle extract but could not establish the presence of (+)-gallocatechin. Instead he (18) (and also White (19, 20)) claimed the presence of *epi*catechin (rotation not indicated). (−)-*Epi*catechin has been shown by Roux and Maihs (12) to be absent from both fresh-bark and commercial wattle extracts, but commercial extract may contain minute traces (paper chromatographic evidence) of (+)-*epi*catechin formed presumably by epimerization of (+)-catechin under the hot conditions used for extraction (21). (+)-Catechin and (+)-gallocatechin undoubtedly constitute the major phloroglucinol-containing "flavonoid" compounds of black wattle extract (21). King (18), from work on impure material, surmised that a 3, 7, 3′, 4′, 5′-pentahydroxyflavan (I) was possibly present in the commercial extract, but he did not isolate the compound nor did he obtain derivatives. Roux and Maihs (12) have estimated the concentrations of these catechins (I, II, and III) in fresh-bark extracts and shown these compounds present in high concentration in the sap of the sieve tubes of the bark (21).

Pigman, Anderson, Fischer, Buchanan, and Browning (22) showed that unidentified anthocyanidins of low absorption maxima (530 mμ) could be generated from wattle tannins. Roux (23, 3) studied light absorption and chromatographic methods for differentiating between anthocyanidins of the resorcinol and phloroglucinol series and showed (3, 5) that two scarlet anthocyanidins were formed from wattle tannins in 5–9% yield (24). These appear to be robinetinidin (VI) (25, 14) and fisetinidin (VII) (16). These anthocyanidins appear to be generated mainly from specific components of high



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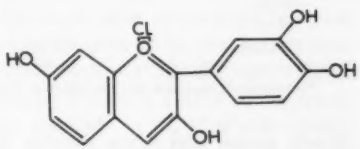


VII

average molecular weight (4), but traces of monomeric flavan-3,4-diols (leucorobinetinidin (V) (25, 14) and leucofisetinidin (IX) (25, 23)) which may also be converted into these anthocyanidins (VI and VII respectively) have been found present (paper chromatography) in some fresh-bark specimens examined (5). The yield of anthocyanidins from similar (V and IX) synthetic leucoanthocyanidins is 37–43% (24), suggesting that leucoanthocyanins constitute some 12–22% of wattle tannins.

Both the catechin chemistry and leucoanthocyanin chemistry of wattle extract show that flavans form the basis of the low- and high-molecular-weight compounds and tannins present.

OCCURRENCE OF CATECHINS IN RELATED WATTLES

Green wattle (*Acacia decurrens*), silver wattle (*A. dealbata*), and golden wattle (*A. pycnantha*) trees, in addition to black wattle (*A. mollissima*), have all been introduced into South Africa from Australia, and the South African wattle industry, although at the moment exclusively concentrated on black wattle, was at one time also associated with the afforestation of green and silver wattles. Golden wattle bark is used for tanning purposes in South Australia, where it is known as "Adelaide bark". Green wattle is capable of exceptionally vigorous growth, and its bark has a tannin content comparable with black, while silver wattle is reputed to be frost-resistant (see Roux (26) for discussion on these wattles). Their bark extractives, however, develop excessive redness on atmospheric oxidation and are therefore considered less suitable for tanning, due mainly to prejudice existing in the tanning industry. Green and silver wattles have been crossed with black in hybridization studies at the Wattle Research Institute, Pietermaritzburg (27), and the distribution of catechins in their bark extracts (21) is, therefore, of exceptional interest.

TABLE I

DISTRIBUTION OF CATECHINS IN VARIOUS WATTLES*

Wattle	(−)-Robinetinidol (I)	(+)-Catechin (II)	(−)-Epicatechin (II)	(+)-Gallocatechin (III)
Black	+++++	++++	−	+++++
Green	+	++++	−	+++++
Silver	(+)	++++	+++++	++
Golden	−	+++	+++++	(+)

*Considerable variation in concentration of catechin components has been found within each species.

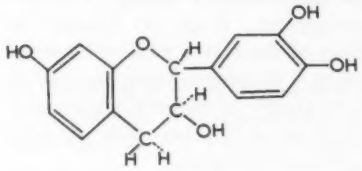
Black, green, and silver wattles have previously been regarded as varietal forms of the same species (*A. decurrens*) (28), and the similar distribution of

catechins in their barks confirms their close relationship. These trees have similar feathery compound leaves, differing widely in appearance from the lanceolate phyllodes of the golden wattle. Golden wattle is obviously furthest removed from black wattle in its botanical characteristics and also in composition of the catechin fraction of the bark (Table I). The additional presence of (−)-*epi*catechin in silver and golden wattle barks is also of interest.

(+) 7, 3′, 4′-Trihydroxyflavan-3, 4-diol (IX) (2, 3-*trans*: 3, 4-*cis*) (29), first isolated by Keppler (30) from *A. mollissima*, has been found present in the heartwoods of golden, silver, and green wattles by Roux (31).

LEUCOANTHOCYANIN CHEMISTRY OF QUEBRACHO WOOD

Quebracho extract was shown by Pigman *et al.* (22) to afford red colorations ($\lambda_{max.}$ = 520 mμ) on treatment with hydrochloric acid in alcoholic solution under pressure. Roux (23) established this pink coloration to be almost entirely due to fisetinidin (VII), but examination of the commercial extract with the aid of synthetic (±) 7, 3′, 4′-trihydroxyflavan-3, 4-diol (23, 25) (IX) failed to show the presence of a monomeric leucoanthocyanidin which could give rise to this anthocyanidin, and it was concluded that only complex polymeric leucofisetinidins were present in the commercial extract.



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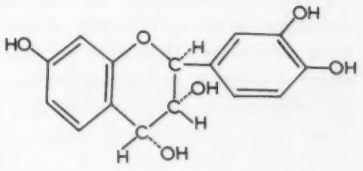


IX

Examination of the cross section of quebracho logs by Roux (32) (submitted July, 1957) showed the presence of a (−) 7, 3′, 4′-trihydroxyflavan-3, 4-diol (IX) which was subsequently characterized in greater detail by Roux (33), Freudenberg and Weinges (4), and Roux and Evelyn (5), and also shown by Clark-Lewis and Roux (29, 34) to be enantiomorphous with (+)-mollisacacidin isolated from wattle wood by Keppler (30). This represents the first occasion on which the presence of enantiomorphous "flavonoid" compounds have been established in nature (29, 34) ,and both these compounds have the 2, 3-*trans*: 3, 4-*cis* configuration of substituent groups in the heterocyclic ring (29, 34, 35). Radial sampling of the wood by Roux (32) showed evidence of the conversion of monomeric into polymeric flavan-3, 4-diols of the leucofisetinidin type. The presence in quebracho wood of (−) 7, 3′, 4′-trihydroxyflavan-3, 4-diol (IX), shown by Roux (33, 5) to be the most important precursor and prototype of quebracho tannins, is of special interest in view of

Freudenberg and Maitland's (16) (1934) almost correct forecast ("quebracho catechin" VIII) of the prototype of these tannins.

At the Fifth International Conference of Leather Chemists in Rome (September, 1957) King and White (36, 37) claimed to have identified the following "flavonoid" compounds from the heartwoods of *Schinopsis* spp., namely, fustin, sulfuretin, (+)-catechin, 2-benzyl-2, 6, 3′, 4′-tetrahydroxycoumaran-3-one and its 4′-methyl ether, leucocyanidin, and leucofisetinidin 3- or 7-glucoside, and they concluded that "hydrolyzable" tannins in the leaves of the quebracho tree were converted into typical "condensed tannins" of the heartwood. No accurate proof of structure of these compounds other than chromatographic evidence was provided in the supporting work by King (18) or subsequently in the literature. Their "amorphous leucofisetinidin 3- or 7- glucoside" is presumably identical to the leucofisetinidin aglycone (IX) characterised by Roux (32, 33), Freudenberg and Weinges (4), and Roux and Evelyn (5).

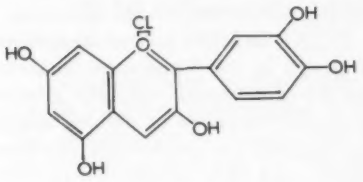
The decline in concentration of the monomeric (−)-leucofisetinidin (IX) from the outer heartwood toward the central heartwood (also noticed by King and White (36)) was shown by Roux and Evelyn (5) to be accompanied by a corresponding increase in emphasis of the lower-RF, higher-molecular-weight tannins, by progressive increase in the average molecular weight of the tannin mixture, by an increase in the percentage of tannins, and by a reduction of the percentage of nontannins present. Roux and Evelyn (38) have also shown that with vertical sampling of the tree a vertical "coning" effect is evident as regards molecular weight, tan/nontan ratio, monomeric leucofisetinidin concentration, and total percentage of fisetinidin generated. These data provided both chemical and biochemical evidence of the presence of flavan-3, 4-diol groups of type IX in quebracho tannins.

Comparison of the yields of fisetinidin from monomeric (−) 7, 3′, 4′-trihydroxyflavan-3, 4-dio (IX) and from various fractions of quebracho extract obtained on radial sampling shows that the extract (containing also carbohydrate sugars) contains the equivalent of 20–40% leucofisetinidins (5, 24). The combined concentration of complex and monomeric leucofisetinidins is apparently highest on the outer edge of the wood and declines gradually in concentration toward the central heartwood. Polymeric forms presumably require breakdown into monomeric flavan-3, 4-diols prior to conversion into the corresponding anthocyanidin. The high concentration of leucofisetinidins in the heartwood at the sapwood/heartwood interface and also throughout the heartwood emphasizes the importance of this monomeric form in relation to the polymeric tannins.

The monomeric leucofisetinidin is almost completely removed from the log by the practice of trimming away the sapwood and outer heartwood in commercial logs to prevent insect attack and is consequently absent from the commercial extract (5).

LEUCOANTHOCYANIN CHEMISTRY OF MANGROVE AND OTHER PLANT EXTRACTS

Alkaline fusion of mangrove bark extract (*Rhizophora mucronata*) under anhydrous conditions (7) yields mainly phloroglucinol and protocatechuic acid. The extract has been shown to be exceptionally rich in leucoanthocyanins (22, 39) affording a 16.5% yield of cyanidin (X) only, which contains



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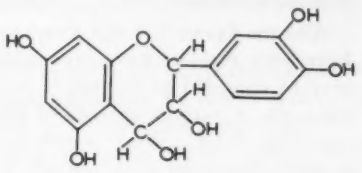
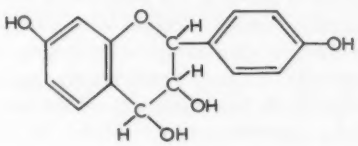


XI



XII

the elements of these degradation products. This suggests that polymeric leucocyanidins of corresponding structure (XI) probably mainly form the basic units in the tannins present. The monomeric leucocyanidin (XI), known from synthesis (40, 13) and recently isolated from natural sources (41), is however absent from spray-dried commercial extract derived from *R. mucronata*.

Roux (42) has shown the association of simple and complex (mol. wt. = 2000) leucoanthocyanins corresponding in basic structure to leucofisetinidin (IX) and leucoguibourtinidin (XII) in the heartwood of *Guibourtia* spp. from tropical Africa. These and other instances (32) of the association of monomeric and polymeric leucoanthocyanins of the same structural pattern lend support to the concept that intact flavan-3, 4-diol structures persist in many complex "condensed" tannins (32, 43, 44) which appear to be ubiquitously distributed in nature (see Bate-Smith (45, 46)).

REACTIVITY OF THE FLAVAN-3,4-DIOL NUCLEUS

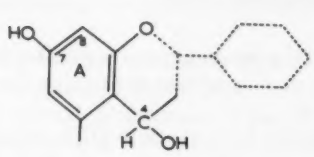
From recent work on wattle and quebracho extracts interesting aspects of tannin chemistry have emerged which were previously discussed by Roux and by Freudenberg at the January, 1959, meeting of the Plant Phenolics Group

in London. (See Freudenberg and Weinges (35) for reference to this discussion). Roux pointed out that tannins may be obtained from freshly cut wattle bark and quebracho wood in an almost colorless (at times cream or very pale pink) state by immediate extraction with methanol in the cold. These colorless tannins already have an exceptionally high degree of condensation (av. mol. wt.: 1250 for wattle, and 600–1750 for quebracho, depending on sampling position), and they are unlikely to have originated from either atmospheric or enzymic oxidation mechanisms as in the case of the phlobatannins associated with (+)-catechin and (−)-*epi*catechin (47–49).

Also the flavan-3, 4-diol structures V, IX, XI, and XII present in tannins have very reactive secondary hydroxyl groups in the 4-positions, as these may be regarded as portion of secondary p-hydroxybenzyl alcoholic groups when the A nucleus consists of either potential resorcinol or phloroglucinol units (see XIII). Such p-hydroxybenzyl alcohols are exceedingly reactive in ether formation with phenols or alcohols, and their reactivity has been thoroughly studied for lignins and lignin model substances (50–54). These reactions occur with loss of water in the presence of HCl, and it appears that condensation of secondary benzyl alcohols with phenols under these conditions might even involve the elimination of hydrogen on the benzenoid ring (see Mayer and Merger (55)). Such reactions give an indication of the reactivity of the 4-hydroxyl in the leucoanthocyanidin units, and it is also known that benzyl ether links, e.g., benzyl aryl ethers (50, 54) are easily split in alcoholic hydrochloric acid. These reactions led the author to the suggestion that ether links between "flavonoid" units through the 4-position of leucoanthocyanidins to the 6- or 8- position of some other or similar "flavonoid" nuclei might be one mode of linkage present in these tannins. Such ether links would split under the conditions (HCl -propan-2-ol) (22) used for the generation of anthocyanidins from tannins to form flavan-3, 4-diol nuclei, which would in turn be converted into the corresponding anthocyanidins. Wattle and quebracho tannins are suspected (15, 56) to contain either ether linkages or else non-reactive tertiary aliphatic hydroxyl groups.

Freudenberg (35), however, pointed out that the alternative of carbon-to-carbon instead of ether links through the same positions would also undergo fission of a well-known type involving the removal of a substituent from its position on a resorcinol or phloroglucinol ring.

The well-known "bisulfiting reaction" of sodium bisulfite and meta-bisulfite with condensed tannins may also be regarded as a reaction of bisulfite with p-hydroxybenzyl alcohols, similar to the well-known "sulfiting reaction" with benzyl alcohols and benzyl ethers as lignin model substances (50–54). The reaction of bisulfite with flavan-3, 4-diol (leucoanthocyanidin) nuclei would undoubtedly involve displacement of the reactive 4-hydroxyl by a sulfonic acid group (XIV); it could also cause hydrolysis of benzyl ether groups if ether groups are present in the 4-position (51, 54). This reaction has an



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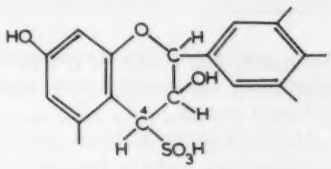
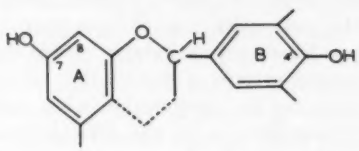


XIV

important bearing on the color reduction and solubility of condensed tannins (see below).

The earlier theory by Freudenberg and Maitland (16) of the mechanism of the HCl-induced condensation of catechins, supported by recent studies of the condensation of flavans with phenols by Brown and Cummings (57), implied recognition (58, 59, 69) of the ether bridge in the heterocyclic ring of flavan-3-ols (catechins) as representing p-hydroxybenzyl aryl ethers (XV), originating from secondary p-hydroxybenzyl alcohols involving the B phenolic nucleus. These benzyl ether links apparently undergo ring fission in catechins



XV

on HCl treatment, and the resulting secondary benzyl alcohol readily condenses with a second catechin or an added phloroglucinol nucleus with water elimination, as shown by Mayer and Merger (55) (see also Brown, Cummings, and Somerfield (69) and Freudenberg and Alonso de Lama (59).)

In catechins (flavan-3-ols) only the p-hydroxybenzyl aryl ether as in XV is present, whereas in monomeric leucoanthocyanidins (flavan-3, 4-diols) both this benzyl ether link (XV) and a secondary benzyl alcohol (XIII) are present. In the presence of HCl the hydroxyl group in the 4-position or that made available in the 2-position may undergo condensation involving water elimination with a hydroxybenzene nucleus to form C-C links or with hydroxyl groups to form ether links. Freudenberg and Weinges (58) and Freudenberg and Alonso de Lama (59) have shown that the presence of hydroxyl groups in both the 7- and 4′- positions are necessary for acid-induced condensations of flavans. The substitution of these key positions with hydroxyl groups probably serves the dual function of (*a*) increasing the labile nature of the benzyl ether group and simultaneously increasing the tendency of the benzyl alcohol

group generated, toward condensation, and (*b*) providing reactive sites on the substituent benzenoid nuclei, usually in p- or o- positions relative to these hydroxyl groups.

Although there is almost certainly no parallel between these HCl-induced condensations and the biosynthetic condensation which may occur through the action of enzymes in heartwoods and barks, the above chemistry nevertheless furnishes an accurate idea of the reactivity of the flavan nucleus. These reactive positions must predict the modes of condensation in tannin biogenesis.

FUNDAMENTAL CHEMISTRY OF CONDENSED TANNINS IN RELATION TO LEATHER CHEMISTRY

Recent work on condensed tannins outlined above has an important bearing on certain aspects of leather chemistry. Roux (60) has found that the pattern of anthocyanidins generated from certain condensed tannins is quite characteristic and may be used for the identification of such extracts in leather even where the extracts have been lightly sulfited, where the leather contains high percentages of inorganic salts (e.g., chrome retan leather), or where the vegetable extracts have been used for lightly "mordanting" chrome leathers. In these cases the normal pattern of distribution of the components of the vegetable extracts may not be recognizable when using paper chromatograms as a means of identification, or else difficulty may be experienced in extracting the tannins from the leather to enable their identification.

Solid vegetable extracts rich in leucoanthocyanidins, e.g., black wattle (and to a greater extent, green, silver, and golden wattles), quebracho, mangrove and the extracts of *Guibourtia* spp., redden rapidly on exposure to sunlight. This reddening effect is evident also for the pure monomeric flavan-3, 4-diols, and it is surmised that both ultraviolet and infrared radiations are responsible for conversion of the leucoanthocyanidin units into traces of scarlet anthocyanidins. This effect was inferred also by Hillis (61) in connection with the redness of tanning extracts derived from many *Eucalyptus* spp.

Bisulfiting is well known in the tanning trade for having a remarkable effect in reducing the darkness and redness of those vegetable extracts which have been exposed to both atmospheric oxidation and light, and also for increasing their solubility. Sulfiting, therefore, probably has the dual function of reducing quinonoid groups and effecting substitution in such a position as to inhibit anthocyanidin formation from the flavan-3, 4-diol groups present in most condensed tannins. This is obvious from structure XIV and the relevant discussion above. Bisulfited tannins for example, show greatly reduced leucoanthocyanidin content as judged from the yields of anthocyanidin pigments obtained before and after bisulfiting (31).

In relation to tanning theory Roux (62) and later Sykes and Roux (63) drew attention to the importance of the nature of the phenolic components of an extract in determining the affinity relationship for such widely differing substrates as cellulose and collagen. This aspect has received further emphasis (64) from the relationship, established by Roux and Evelyn (2), between the RM [log ($^1/_{R_F}$ − 1)] value of tannins fractions from wattle and quebracho and their number average molecular weight. It is evident that the average molecular weight of the tannin fraction, its chemical nature, and swelling of collagen (70), probably represent greater factors in the tannin-collagen affinity relationship than considerations of "active sites" on the collagen chains. The chemical affinity of tannins for any given substrate increases progressively with increasing molecular weight (64, 1, 2) as was previously speculatively surmised by Page (65) on the basis of his "gelatin numbers". When considering the heterogeneous nature of vegetable extracts in relation to molecular weight (1, 2), the use of such extracts for studies of the "mechanism of tannage" could lead to incorrect conclusions regarding "active sites", where these conclusions are based on such physical phenomena as "degree of fixation" and "lowering of the shrinkage temperature of collagen".

Condensed tannins present in wattle extract contain high percentages of orthohydroxy phenolic groups and show absorption behavior in the ultraviolet spectrum ($\lambda_{max.}$ = 203 and 280 mμ) which is typical of catechins (flavan-3-ols) and leucoanthocyanidins (flavan-3, 4-diols) and also of their constituent phenols. These factors are the basis for rapid and accurate photometric methods (66, 67) for determining tannin content, preferable in many respects to the empirical hide-powder method (68).

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Offences against common justice listed in 1648 by the Judge of Assize for the Northern Circuit (England) included the following of particular concern to tanners:

If he set his Fats (vats) in Tan-hills [mounds to warm the liquor, hastening the tanning process at the expense of quality]

If he over-lime his Hide

If he tan any Leather in warm Owze [ooze or wooze—the tanning liquor]

If he do not work the Lime well out of the Leather

If he use any stuff but Malt, Meal, Tapwort, Hen-dung, Culver-dung, Ash-bark, and Oak-bark [Culver: pigeon; Tapwort: dregs, probably of beer]

If he use any deceitful Mixture for raising his Hides

If he suffer his Hides to be frozen with Winter-frost, or to be parched with summer-sun, or to be dried by the Fire.

If he tan any rotten hides

If he do not renew his Owze so often as Need requires

If he do not keep his Soal-leather twelve Months, and upper-leather nine months in the Owze.

If he sell any tanned Leather out of a Market

If he sell any tanned Leather, which is insufficiently tanned

If he sell any tanned Leather, before it be searched and sealed

If any Tanner be a Currier or a Shoemaker, or use any other Trade which cuts Leather, or *e contra*.

—*Leather in Life, Art and Industry.* J. W. Waterer. London: Faber and Faber, Ltd., 1946.

A DIALDEHYDE STARCH PRETANNAGE FOR RAPID TANNING OF SOLE LEATHER*

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ABSTRACT

A sole leather tannage is described consisting of a pretannage with dialdehyde starch followed by a rapid vegetable tannage in strong liquors. Chemical and physical data on the finished leather indicate that it is quite similar to commercial sole leather.

—x—x—

INTRODUCTION

The current tanning of heavy leather with vegetable tannins is a relatively long process. Although the time of tannage has been shortened somewhat by greater chemical control and mechanical improvements, several weeks are still required. A rapid and economical method of tanning would be of advantage to the industry.

Attempts have been made to shorten the time by the use of strong liquors, mechanical action, pH control, and control of the acid and salts content as described by Kay (1). The use of stronger liquors and mechanical action, such as drumming, accelerates the tanning process but has a tendency to damage the leather, usually causing "pebbling of the grain". It has been found that if leathers are given a pretannage with various inorganic or organic materials (chromium, syntans, etc.), this pebbling effect may be minimized. One of the materials that has been used in this manner is formaldehyde. The principles of the aldehyde tannage are described by Mellon (2), who also gives a complete bibliography.

There are only a few references to the pretannage of vegetable-tanned leather with formaldehyde, although numerous tannery experiments have been run. It has been found that this pretannage protects the leather from drawn grain in subsequent drumming and, in addition, accelerates the rate of penetration of tannin into the hide. The resulting leather is predominantly of the vegetable-tanned type, showing little effect of the formaldehyde pretannage (3, 4). This pretannage, although successful in accelerating vege-

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table tannage, has serious disadvantages, so that it is seldom used. Formaldehyde is unpleasant and somewhat dangerous to work with, and the finished leather has a tendency to be hard, flat, tinny, and cracky.

Within the last few years other types of aldehydes have been found to have tanning properties. Some of the dialdehydes are of particular interest. Seligsberger, Mann, and Clayton (5, 6) have recently reported on the use of glyoxal as a pretannage for a lignosulfonate tannage. These authors also give data obtained with other aldehydes, including dialdehyde starch supplied by this Laboratory. A preliminary report from this Laboratory on the tanning power of dialdehyde starch has been presented (7). Dialdehyde starch is a polyfunctional aldehyde derived from starch by periodate oxidation (8, 9, 10). These investigations indicated that this material might have advantages over formaldehyde as a pretanning agent. Preliminary tests on small pieces of hide in battery jars were promising and were continued on a larger laboratory scale. The latter will be discussed in this paper.

In these tests we have not attempted to produce a new type of leather but to produce an established type of leather by a shorter process.

EXPERIMENTAL

Outline of Procedure

A. Hide Preparation

1. Unhaired by conventional lime-sulfide
2. Washed for ½ hr. in drum with running water or for 2 hr. in a still vat
3. Adjustment of pH
   a. In pH 4.5 buffer overnight; or
   b. Drum for 4 hr. with 2% ammonium chloride (pH 8.5–9.0) 0.1% Oropon N*

B. Pretanning with Dialdehyde Starch

1. Tanning liquor:
   Sodium sulfate—8% (solution basis)
   Sodium bicarbonate—6.3% (white-weight basis)
   Water—300 to 500% (white-weight basis)
   Dialdehyde starch—5, 10, or 15% (white-weight basis)
2. Tanning conditions
   a. In drum—7 to 16 hr.
   b. In still vat—1 to 2 days

*The mention of trade names or companies throughout this paper does not constitute an endorsement by the Department of Agriculture over other products of a similar nature not mentioned.

C. Vegetable Retannage

1. Tanning liquor
   a. Blend of quebracho and chestnut extracts
   b. Tannin concentration—14 to 15%
   c. pH—3.8 to 4.2
2. Tanning conditions
   a. In drum—8 hr. drumming and 16 hr. standing
   b. In still vat—4 to 5 days

D. Finishing

The leather was wheel-extracted, bleached, oiled, loaded, and rolled in the conventional manner.

Details of Procedure.—For each test one side of a hide which had been unhaired in the laboratory by a lime-sulfide process was cut into bend, belly, and shoulder. These were washed in a drum for ½ hr. with running water or left in still water for 4 hr. After the washing they were brought to the desired pH. Preliminary tests had shown that this pH could vary over a range of 4.5 to 9.0 with apparently satisfactory results in dialdehyde starch tannage. A tannage at approximately pH 4.8, near the lower level, and one at approximately 8.5, near the upper level, were selected for these tests.

To bring the hides to pH 4.8 they were treated by immersion for at least 24 hr. in a solution of 10% sodium chloride, 3.5% sodium acetate, and 1.8% glacial acetic acid, using a solution-to-hide ratio of 3 to 1. For the pH level of 8.5 the hide pieces were drummed slowly for 4 hr. in a solution of 2% ammonium chloride and 0.1% Oropon N (on the white-hide weight) with a ratio of 3 to 1. The interior of the hide was then about pH 8.5 and the surface about 8.0. After the pH was adjusted, the hide pieces were washed with running water in the drum for ½ hr.

The hides were pretanned by suspending in a 300–500% volume of an 8% sodium sulfate solution containing 6.3% sodium bicarbonate and either 5, 10, or 15% dialdehyde starch (on the white-hide weight). This was preferably made up as a stock solution several times this strength. The calculated amounts of sodium sulfate and sodium bicarbonate were added to the water which was only slightly above room temperature. After these were dissolved by stirring, the dialdehyde starch was added in several portions. After a further stirring of about ½ hr. the dialdehyde starch was partially dissolved, the balance being in a highly dispersed suspension. When diluted for use the pH ranged from 7.8 to 8.4.

The dialdehyde starch pretannage was conducted either in a drum or in a still vat. The wooden drum used was 56″ in diameter and 26″ wide. It was

equipped with a variable speed drive to operate between 2 and 20 rpm. The hide pieces were drummed intermittently for 7 hr. at the lowest speed. If at this time the shrinkage temperature was 75°–80°C., and there was only a slight, dark, shrunken streak in the center of the hide, it was considered ready for vegetable tanning. If these conditions were not met, the leather was left overnight without motion.

In the still vat pretannage the pieces were suspended in a copper-lined vat with a liquor-to-hide ratio of 5 to 1. Penetration in this vat required 24 to 48 hours. The proper duration was determined as before by shrinkage temperature measurements.

The pieces of hide pretanned by either of the above methods were washed in running water for ½ hr. prior to entering the vegetable tanning liquor. The vegetable retannage was carried out in either a drum or in a still vat. The tanning liquor was made up to contain 14 to 15% tannin from a blend of 50% clarified quebracho extract and 50% imported chestnut extract (on a tannin basis). The liquor was used for a total of 20 times with appropriate strengthenings to maintain the tannin content. The pH was maintained at approximately 4.0. After each test the liquor was settled, and abou 10% of the volume (equal to 7 to 8% of the original tannin content) was discarded before strengthening for the next test. The dialdehyde starch liquors were made fresh for each tannage. Penetration was rapid in the drum, being complete either in 8 hr. drumming or by this drumming followed by standing 16 hr. In the still vats penetration required 3 to 5 days. In each case the leather was washed for 10 to 15 min. and was then ready for extracting and finishing.

Some of the leathers were extracted, bleached, oiled, and finished at a commercial tannery. When returned to the laboratory the leathers were analyzed and tested for physical properties by the Official Methods of the American Leather Chemists Association (11) where possible.

RESULTS

The variables involved in these tests will be considered first as to their immediate effects, and secondly as to their apparent effects upon the finished leather. No immediate effects were noted by the variation in the pH values of the hides before tanning. As judged by shrinkage temperature determinations, each pH tested gave good penetration and fixation of the dialdehyde starch. The variations in the amounts of dialdehyde starch used resulted in changes in penetration and fixation of the dialdehyde in proportion to the amount used.

A comparison of drum tanning with vat tanning shows that penetration and fixation of the dialdehyde starch are much more rapid in the drum. However, in our tests, drum tanning caused a raised grain and pebbling. For the vegetable tannage, drum tanning is again much more rapid than vat

tanning with little danger of pebbling, except for a moderate amount on hides pretanned with only 5% dialdehyde starch.

The vegetable tanning liquors were kept at approximately the same tannin content and pH. The barkometer increased gradually and the purity decreased with the reuse of the liquors. These variations had little measurable effect on the rate of penetration or fixation of the tannin.

Table I shows the analyses of the vegetable tanning liquors; Table II shows the uptake of tannin from some of these liquors.

TABLE I

ANALYSES OF VEGETABLE LIQUOR USED FOR RETANNAGE OF DIALDEHYDE STARCH-PRETANNED HIDES

Expt. No.*	Barkometer Degrees	Total Solids %	Soluble Solids %	Tannin %	Purity Tan/SS × 100	pH
1	75	18.7	18.5	14.7	79.5	3.7
2	78	18.2	18.0	13.9	77.2	3.8
3	78	18.6	18.5	13.9	75.5	3.9
4	78	18.5	18.3	13.7	74.5	4.0
5	81	19.3	19.1	14.2	74.7	4.1
6	88	21.2	20.9	15.7	75.4	3.7
7	75	18.5	18.2	14.0	76.5	3.9
8	81	19.4	19.1	13.9	72.7	4.7
9	93	22.0	21.6	14.9	68.9	4.2
10	90	21.1	20.6	13.7	66.2	4.2
11	94	22.0	21.7	14.1	65.1	—
12	95	21.9	21.7	13.8	63.6	4.2
13	100	23.1	22.7	14.8	65.1	4.2
14	102	23.4	23.2	15.1	65.1	4.2
15	104	23.3	22.9	14.2	62.1	4.1
16	104	23.7	23.3	14.6	62.7	4.1
17	109	25.1	24.8	16.1	65.0	4.1
18	105	23.8	23.4	14.9	63.6	4.2
19	105	23.9	23.4	14.3	60.9	4.1
20	103	23.5	23.2	14.3	61.6	4.2
21	108	24.4	24.1	14.9	61.8	4.2

*Sampled immediately before each use.

All the leathers had a good color and general appearance, being well-filled and moderately flexible, and showing no tendency for the grain to crack.

Some typical analyses of the leathers are shown in Table III. These indicate that the variations in tanning methods have had little effect upon the final analytical values. They also indicate that these leathers are comparable analytically with sole leather of current production.

TABLE II

UPTAKE OF TANNIN FROM VEGETABLE LIQUORS
BY DIALDEHYDE STARCH-PRETANNED HIDES

Expt. No.	Sappage of Tannin from Liquor %	Weight of Liquor g.	Sappage of Tannin g.	White Hide Weight g.	Uptake of Tannin/100g. White Hide g.
2	5.57	80,000	2,856	9,600	29.8
3	4.16	54,000	2,246	9,092	24.7
4	3.66	54,000	1,976	9,675	20.4
5	4.52	54,000	2,441	9,532	25.6
6	3.72	56,000	2,083	8,990	23.2
7	5.33	80,000	4,264	20,600	20.7
8	4.57	80,000	3,656	17,200	21.3
9	3.95	80,000	3,160	19,600	16.2
10	3.51	80,000	2,808	18,000	15.6
11	5.21	80,000	4,168	16,800	24.8
14	4.93	80,000	3,944	19,600	20.1
15	5.15	80,000	4,120	19,170	21.5
16	3.56	80,000	2,840	16,200	17.6
17	3.17	80,000	2,536	15,925	15.9
18	3.15	80,000	2,520	16,570	15.2
19	3.23	80,000	2,580	14,800	17.5
20	3.18	80,000	2,540	14,900	17.0
21	3.18	80,000	2,128	13,500	15.9
				Average	20.2
				Standard Deviation	± 4.2

Table IV gives the results of physical tests upon the finished leathers—tensile strength, elongation, grain crackiness, piping, compressibility, rate of abrasion, and water absorption. For comparison, data from comparable leathers from three commercial tanneries are also given. In all cases the values are quite comparable, and all conform easily to federal specifications.

DISCUSSION

An interesting property of the dialdehyde starch pretannage step is the variation permissible in the condition of the hide before entering the tanning liquor. In most tannages it is necessary to condition the hide to retard fixation of the tanning material until penetration is accomplished. This is not necessary with the dialdehyde starch pretannage. A simple deliming process with ammonium chloride and a light bating are sufficient.

For the pretannage apparently 5% dialdehyde starch is sufficient. The properties of the finished leather are predominantly those of a vegetable-tanned leather, and the purpose of the dialdehyde starch pretannage is

TABLE III

ANALYSES* OF DIALDEHYDE STARCH–PRETANNED VEGETABLE SOLE LEATHERS (BENDS)

			Expt. 19	Expt. 16		Expt. 3		Expt. 6
State of tannage	Rough†	Finished	Finished	Finished	Finished	Finished	Finished	Finished
Method of pretannage	Vat	Drum	Vat	Vat	Vat	Drum	Vat	Drum
Method of vegetable tannage	Drum	Drum	Vat	Vat	Vat	Drum	Drum	Drum
Method of deliming	Buffer	Buffer	NH_4Cl	NH_4Cl	Buffer	Buffer	Buffer	Buffer
Dialdehyde starch used, %	15	5	5	10	15	15	15	20
Moisture, %	8.8	9.8	8.3	8.8	11.7	12.0	9.8	12.2
Petroleum ether extract, %	3.6	7.4	8.5	6.9	8.9	6.7	4.2	5.8
Insoluble ash, %	0.2	0.3	0.2	0.2	0.1	0.1	0.5	0.1
Hide substance, %	44.6	33.7	34.2	35.9	33.1	33.1	36.8	33.2
Soluble matter, %	10.8	25.5	26.2	24.2	21.1	22.0	24.1	21.7
Combined tannin, %	32.0	23.3	22.6	24.0	25.1	26.1	24.6	27.0
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Degree of tannage	72.3	68.9	66.0	66.8	76.0	78.9	67.0	81.4
Soluble nontannin, %	2.6	17.8	17.5	16.4	12.7	13.9	17.0	13.0
Uncombined tannin, %	8.2	7.7	8.7	7.8	8.4	8.1	7.1	8.7
Total ash, %	0.2	5.8	5.5	5.2	3.9	4.3	5.4	4.0
pH value	——	3.7	3.7	3.8	3.8	3.8	3.2	3.9
Gain—white weight to finish, %	48.3	67.3	72.0	73.1	70.2	72.2	——	75.0

*All analyses calculated on the "as received" basis.
†After tanning at laboratory and before finishing.

TABLE IV

PHYSICAL PROPERTIES OF DIALDEHYDE STARCH–PRETANNED VEGETABLE SOLE LEATHER COMPARED WITH COMMERCIAL PRODUCTION

Bend No.	Tensile Strength[a] Thickness in.	Tensile Strength lb./in.²	Elongation at[b] Break %	Elongation at[b] 200 lb. Load %	Grain Cracking[c] Mandrel Diameter[h] 16ths of an Inch A[k]	Grain Cracking[c] Mandrel Diameter[h] 16ths of an Inch B[k]	Piping[d] Mandrel Diameter[i] 16ths of an Inch	Compressibility[e] %	Abrasion[f] Loss in Weight, grams[j] Range	Abrasion[f] Loss in Weight, grams[j] Average	Water Absorption[g] Water absorbed after ½ hr. %	Water Absorption[g] Water absorbed after 2 hr. %	Water Absorption[g] Water absorbed after 24 hr. %
Dialdehyde Starch Pretanned–Vegetable Sole Leathers													
1	0.217	3,280	24	21	10	10	3	11.3	1.00–1.16	1.06	26.8	42.3	56.2
2	0.189	3,840	25	22	6	5	3	14.6	0.97–1.44	1.13	29.6	45.4	58.2
3	0.214	3,390	25	22	8	7	3	13.3	1.28–1.51	1.39	23.4	40.6	52.2
4	0.214	3,060	22	21	8	7	4	10.4	1.19–1.51	1.45	23.0	38.9	49.0
5	0.210	3,400	23	21	10	8	10	10.5	1.09–1.27	1.16	20.4	32.7	42.7
Average								12.0		1.24	24.6	40.0	51.7
Commercial Vegetable Sole Leathers													
1	0.239	3,320	17	15	12	10	14	9.7	1.13–1.49	1.30	27.0	48.9	61.0
2	0.213	3,780	27	17	8	8	16	8.2	0.95–1.64	1.41	21.2	32.5	45.7
3	0.214	3,390	24	20	8	8	14	13.2	1.46–1.74	1.55	21.9	41.9	54.1
4	0.200	3,150	25	21	10	8	12	12.0	0.96–1.42	1.20	26.6	43.1	56.7
Average								10.8		1.36	24.2	41.6	54.4

[a] ALCA Method E15. Test strips were 1 cm. wide. Each value is the average of 10 determinations.
[b] ALCA Method E17. Test strips were 1 cm. wide. Each value is the average of 10 determinations.
[c] ALCA Method E41 with modified mandrels. Samples ranged between 5.0 and 6.0 mm.
[d] ALCA Method E40 with modified mandrels. Samples ranged between 5.0 and 6.3 mm.
[e] ALCA Method E45. $\text{Compressibility} = \frac{\text{original thickness—compressed thickness}}{\text{original thickness}} \times 100$
[f] Measured on a cylinder 8″ in diameter covered with standard abrasive cloth and rotating at 100 rph. Leather pieces held against cloth by a weight of 250 g.
[g] ALCA Method E30. Reported as percentage of initial weight.
[h] Maximum diameter at which grain cracking was observed.
[i] Maximum diameter at which piping was observed.
[j] Grams of leather abraded from a 1-inch square by 400 revolutions of abrading cylinder. Ten samples were tested from each bend.
[k] Two samples taken from each leather adjacent to "A" sampling position.

merely to accelerate the rate of vegetable tanning. Therefore, a high level of dialdehyde starch pretannage is not necessary.

It would be advantageous to reuse the dialdehyde starch liquors by restrengthening, thereby saving some of the dialdehyde and all the other chemicals used. Preliminary tests indicate that the liquors may be restrengthened by adding 4% of dialdehyde starch and used in this manner for at least five times. Further confirmation is necessary.

The results indicate that the complete tannage could be carried out in rocker vats with limited motion. If drums or paddles are available, the time may be considerably reduced. In this case care must be taken to avoid pebbling during the pretannage with dialdehyde starch.

One of the difficulties of rapid tanning with strong vegetable liquors has always been the disposal of the liquors after tanning. For economical reasons it is necessary to reuse this liquor, but by continued reuse it loses its tanning power. The results indicate that the liquors used in this tannage reached an equilibrium and were still suitable for tanning with the loss of no more tannin than is lost in the tail liquors of conventional tannages.

The analytical results obtained on these leathers compare very favorably with those of commercially tanned sole leather. Since the tannage gives leather which is somewhat more flexible than normal, it should be capable of producing a highly flexible leather, if desired. Some yield may have to be sacrificed, as usually occurs in making flexible leather. The physical tests are of interest mainly in showing that the leathers are normal. There was no evidence of the stiffness, flatness, or crackiness usually associated with aldehyde-pretanned leathers. The water absorption property is normal, showing that the high rate of absorption of leather tanned with dialdehyde starch alone is not carried over into the vegetable tannage. The rate of abrasion appears satisfactory, although this measurement suffers from the defect common to all such measurements in that it is measured at only one abrasive force, whereas leather in practice is subjected to a variety of abrasive forces.

The economic feasibility of this process will depend upon balancing the cost of the extra material against the time saved. It will also depend upon the adaptation of the process to tannery equipment. To determine these points a large-scale tannery test is planned.

SUMMARY

It has been shown that a pretannage of heavy hides with a minimum of 5% dialdehyde starch on the white weight permits a rapid vegetable retannage using strong liquors.

The results indicate that regular tannery equipment may be used. Rocker vats appear to give suitable results for both the pretannage and the vegetable retannage. For a more rapid tannage, drums or paddles may be used, taking

precautions to avoid pebbling in the early stages of the dialdehyde starch pretannage.

The tests indicate that the vegetable tanning liquors may be reused repeatedly after discarding about 10% of the sap liquor, strengthening with fresh extract, and adjusting the pH to the proper level. At the point of equilibrium, the purity, penetration, and fixation of tannin are still satisfactory. The complete tannage requires a maximum time of seven days.

The data indicate that this leather is comparable with standard vegetable-tanned sole leather.

ACKNOWLEDGMENTS

We acknowledge with thanks the cooperation of the Northern Utilization Research Laboratory, U. S. Department of Agriculture, for the dialdehyde starch used in our tests and of Armour Leather Company for finishing and evaluating the leathers.

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DISCUSSION

J. F. WAGONER (Armour Leather Company): Mrs. Happich is to be congratulated on a very fine presentation. The data which she has presented reflect the quality of the work which we have learned to associate with the group at Eastern Regional Laboratory. The prime objective of this work has been to determine if leather comparable to commercial sole leather can be produced in a shorter period of time. Therefore, it is of particular interest,

as we are always endeavoring to effect a reduction in the time required for making sole leather.

In recent years the possibility of using the aldehydes as pretanning agents has come in for considerable study. The possible use of dialdehyde starch in this connection certainly merits our serious consideration. And I believe it is of particular interest at this time inasmuch as we are dealing with a comparatively new product which is only now beginning to approach production-scale levels.

The chemical analyses and the physical test data developed on these leathers, which have been produced on a laboratory-scale basis, seem to indicate that there is a good possibility of producing sole leather which compares very favorably with present-day sole leather. The work described provides a good foundation on which to proceed on the larger-scale testing that is necessary to evaluate the process fully from a technical and economic standpoint.

In examining the data it is interesting to note that with the reuse of the vegetable tanning liquor, there was an apparent decrease in tannin consumption, and yet the yields of leather based on the white weight are approximately the same.

I would like to ask Mrs. Happich for her views on this and also if she has any indication that there would be any marked decrease in the amount of vegetable tannins required to accomplish this tannage.

MRS. HAPPICH: The pickup of tannin as recorded was the pickup of tannin from our liquors. These leathers were extracted and finished in a commercial tannery afterward, where the yields became approximately the same. There was considerable tannin pickup by the leather during extracting.

MR. WAGONER: And do you feel that the data indicate that there would be a marked decrease in the amount of the vegetable tannins with dialdehyde pretannage?

MRS. HAPPICH: We do not have enough data to come to any conclusions on that at this time.

DR. LUDWIG SELIGSBERGER (U. S. Quartermaster Research and Engineering Center): Was the temperature in the drum measured? And if the drumming was continued for seven hours in the drum tannage, was the dialdehyde starch stable when the drum was heating up to maybe 90° to 95°F., or did losses occur?

MRS. HAPPICH: We were tanning only one side to a moderate-size drum, Dr. Seligsberger, and the increase in temperature was not very great.

DR. SELIGSBERGER: You don't think the drawn grain came from the action of the drum itself, without temperature increase?

MRS. HAPPICH: Yes, we think from the mechanical action.

DR. SELIGSBERGER: You would probably not need seven hours continuous drumming; I found with other aldehydes that it is not necessary to drum so much.

MRS. HAPPICH: That could be true. We drummed intermittently, also.

JOHN H. DAVIS (Marathon Corporation): I am interested in reuse or restrengthening of the vat liquors. You restrengthened and used them 20 times. What happens to that liquor after it has been used that length of time? Do you throw it away and start all over?

MRS. HAPPICH: We ended our experiment there; however, these liquors had apparently come to equilibrium, and we could have continued to use them. We think that there is a possibility that the discarded liquor could be used in making up the extracting liquor.

A modern educational system should not only sharpen the intellectual capacities and curiosities of each new generation, should not only extract the essential core from ever-accumulating stores of knowledge, should not only find ways to produce new leaders equipped to add to these stores and to create all the new tools that the civilization requires; it must also produce citizens and leaders who will know how to use the knowledge and tools to advance social and cultural life.
—*Education for the Age of Science*, President's Science Advisory Committee, 1959.

We must educate more, and especially we must educate better scientists and engineers. But this is not enough. We must have trained specialists in many fields. Even then we would not be successful if, having such specialists, the American people were merely to applaud and reward them for their contributions while still thinking of them as useful strangers, dimly understood and more feared than admired. Hence, we must also cultivate a widespread dedication to and respect for learning in all fields, and a deep understanding between the public and the experts.
—*Education for the Age of Science*, President's Science Advisory Committee, 1959.

THE USE OF FISH OILS FOR FATLIQUORING LEATHER

III. SUITABILITY OF OCEAN PERCH, HERRING, SALMON, AND MENHADEN OILS IN FATLIQUORING

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ABSTRACT

Although cod oil is used for fatliquoring leather, the oils of ocean perch, herring, salmon, and menhaden are not used extensively by the leather industry. In the present study, fatliquoring with ocean perch, herring, salmon, and menhaden oils produced leathers with about the same amount of extractable grease and the same firmness as did fatliquoring with cod oil. Though not conclusively proven, there was some evidence that the surface of leather fatliquored with the oil of cod was softer than that fatliquored with the oils from the other fish. All the oils investigated, including cod, produced yellowing of the leather surfaces. None produced gummy spew on the leather. Thus the leathers fatliquored by the oils of ocean perch, herring, salmon, and menhaden were similar to those fatliquored by cod, except possibly for surface hardness.

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INTRODUCTION

Although cod oil has long been used in the manufacture of leather, other fish oils have not been employed extensively for such usage. Under the sponsorship of the United States Fish and Wildlife Service an investigation was undertaken at the Tanners' Council Laboratory to study the potential uses in the leather industry of oil from ocean perch, herring, salmon, and menhaden.

To give the research specific direction, fatliquoring was the leather process selected for study. There were two reasons for this choice: (*a*) Since the oil

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†The research reported in this paper was conducted by Tanners' Council Laboratory, University of Cincinnati, under a contract with the U. S. Fish and Wildlife Service. It was financed with funds available under provisions of Public Law 466, 83rd Congress, approved July 1, 1954, generally termed the Saltonstall-Kennedy Act.

content of fatliquored leather is low compared with stuffed leather, the danger of gummy spews would be decreased. (*b*) The high proportion of sulfated oil mixed with raw oil in the fatliquoring operation is such that the possibility of an excessively firm leather produced by the polymerization properties of some raw fish oils also would be decreased, because sulfated oil is much less susceptible to polymerization and oxidation.

The fatliquoring properties of menhaden oil were reported in a previous article (2). The present paper reports the results obtained with ocean perch oil, herring oil, and salmon oil.

In the previous study, leather fatliquored with menhaden oil was compared with that fatliquored with cod oil; cod oil already is used in the leather industry. Chrome-tanned leathers fatliquored in the laboratory and in the pilot plant with menhaden oil and cod oil fatliquors were similar in firmness, surface hardness, tensile strength, and tear strength. Both leathers showed yellowing but no gummy spew and had a similar decrease in amount of extractable grease upon aging. Menhaden oil fatliquor therefore was considered to be similar to cod oil fatliquor. Accordingly, in the present study leathers fatliquored both with menhaden oil and cod oil were used as a basis for judging and comparing the properties of leathers fatliquored with the oils from ocean perch, herring, and salmon.

The properties studied were extractable grease, firmness, surface hardness, yellowing, and gummy spew. Tensile strength, tear strength, and stress-strain measurements were not investigated, since there was no indication that these properties of leather would be altered significantly under the fatliquoring conditions selected.

In the sulfation of fish oils the reaction for an oil like menhaden is somewhat difficult to control. In the earlier studies at the Tanners' Council Research Laboratory on the sulfation of menhaden oil, it was found that the reaction could be controlled better if the sulfuric acid was diluted with phosphoric acid. Four processes were studied. In these processes 200 g. of raw oil was sulfated with the following acid systems:

Process 1: 40 g. of 95% sulfuric acid
Process 2: 40 g. of 95% sulfuric acid mixed with 6 g. of 100% phosphoric acid
Process 3: 40 g. of 95% sulfuric acid mixed with 20 g. of 100% phosphoric acid
Process 4: 40 g. of 95% sulfuric acid mixed with 10 g. of polyphosphoric acid of ortho equivalent of 115%

These four processes were used in studying the sulfation of fish oils, and sulfated oils so prepared were used in this present work.

With so many variables under consideration, this experiment was necessarily somewhat complex. Its specific objectives, in brief, were to determine

how the extractable grease, firmness, surface hardness, yellowing, and gummy spew of leathers fatliquored by oils of ocean perch, herring, and salmon sulfated by processes 1 to 4 compare with these properties of leather fatliquored with menhaden and cod oils sulfated by the same processes.

TABLE I

ANALYTICAL DATA ON RAW OILS USED IN SULFATION EXPERIMENTS I, II, AND III

Raw Oil	Iodine No.	Saponification No.	Fatty Acid No.
Ocean Perch	119	184	4.98
Herring	131	191	5.12
Herring	139	184	4.42
Salmon	166	185	5.28
Menhaden	152	—	—
Menhaden	176	197	11.32
Cod	176	189	29.35

TABLE II

CHEMICAL ANALYSES OF SULFATED FISH OILS IN SULFATION EXPERIMENT I

RAW OIL		SULFATED OIL				
Kind Sulfated	Iodine No.	Sulfation Process No.*	Combined SO_3 %	Total Acid No.	Moisture %	pH 5% Solution
Ocean perch	119	1	6.33	56.78	21.82	5.9
Herring	131	1	5.82	47.54	24.23	6.0
Herring	139	1	5.85	45.23	23.07	5.9
Salmon	166	1	5.57	41.95	29.68	5.9
Menhaden	152	1	5.59	40.15	30.05	6.1
Menhaden	176	1	4.60	34.17	25.61	5.8
Ocean perch	119	2	5.85	58.32	21.17	5.8
Herring	131	2	5.77	48.57	23.62	5.9
Herring	139	2	5.42	41.54	25.20	5.9
Salmon	166	2	5.32	40.76	28.77	6.0
Menhaden	152	2	5.24	34.86	25.79	6.2
Menhaden	176	2	4.63	38.17	27.11	6.0

*Process 1—Oil was sulfated with concentrated sulfuric acid.
Process 2—Oil was sulfated with a mixture of 100% phosphoric acid and concentrated sulfuric acid.

EXPERIMENTAL

In Part II of this series, three experiments were devised to compare methods of sulfation. The comparisons were as follows:

Sulfation experiment I—process 1 versus process 2
Sulfation experiment II—process 2 versus process 3
Sulfation experiment III—process 1 versus process 4

The raw oils and sulfated oils used in those studies also were used in the present study. Data on the raw oils are given in Table I, and data on the sulfated oils are given in Tables II, III, and IV. A description of the methods of analyses and sulfation used is given in Part II of this series (2).

TABLE III

CHEMICAL ANALYSES OF SULFATED FISH OILS USED IN SULFATION EXPERIMENT II

RAW OIL		SULFATED OIL				
Kind Sulfated	Iodine No.	Sulfation Process No.*	Combined SO_3 %	Total Acid No.	Moisture %	pH 5% Solution
Ocean perch	119	2	5.13	74.44	18.42	5.70
Herring	131	2	4.34	56.22	18.80	5.50
Salmon	166	2	4.77	56.70	23.84	5.40
Menhaden	176	2	5.09	34.57	29.43	5.40
Menhaden	176	2	4.55	39.90	27.31	5.50
Cod	176	2	3.79	65.05	14.61	5.50
Ocean perch	119	3	4.20	61.09	18.86	5.50
Herring	131	3	4.37	60.29	20.46	5.30
Salmon	166	3	4.24	47.97	25.88	5.90
Menhaden	176	3	4.20	40.08	26.62	5.70
Menhaden	176	3	3.96	53.99	23.88	5.40
Cod	176	3	3.27	74.89	12.34	5.60

*Process 2—On the basis of 100 g. of oil, the oil was sulfated using a mixture of 20 g. concentrated sulfuric acid and 3 g. of 100% phosphoric acid.
Process 3—On the basis of 100 g. oil, the oil was sulfated using a mixture of 20 g. concentrated sulfuric acid and 10 g. 100% phosphoric acid.

Design of experiments.—To correspond to these three sulfation experiments, three fatliquoring experiments were devised in the present study. Each fatliquoring experiment was a Latin-square, split-plot design.

For each experiment six chrome-tanned kipskins in the blue were sampled as shown in Fig. 1. Six 14″ blocks were cut from each side of the hide. The position blocks were designated by the numbers 1 to 6. In Fig. 1, for example, A-1 means position 1.

TABLE IV

CHEMICAL ANALYSES OF SULFATED FISH OILS USED IN SULFATION EXPERIMENT III

RAW OIL		SULFATED OIL				
Kind Sulfated	Iodine No.	Sulfation Process No.*	Combined SO_3 %	Total Acid No.	Moisture %	pH 5% Solution
Ocean perch	119	1	5.38	53.56	18.30	5.40
Herring	131	1	5.40	54.92	22.70	5.60
Salmon	166	1	5.32	58.92	21.72	5.50
Menhaden	176	1	4.94	42.07	26.79	5.80
Menhaden	176	1	4.78	37.10	28.04	5.80
Cod	176	1	4.20	57.77	18.02	5.70
Ocean perch	119	4	5.70	77.14	19.34	5.40
Herring	131	4	5.74	65.92	21.66	5.60
Salmon	166	4	5.58	55.67	27.03	5.60
Menhaden	176	4	5.54	48.69	29.09	5.50
Menhaden	176	4	5.38	41.54	29.85	5.70
Cod	176	4	4.58	62.69	18.64	5.70

*Process 1—On the basis of 100 g. oil, the oil was sulfated using 20 g. concentrated sulfuric acid.
Process 4—On the basis of 100 g. oil, the oil was sulfated using a mixture of 20 g. concentrated sulfuric acid and 5 g. polyphosphoric acid (ortho equivalent=115%).

TABLE V

DISTRIBUTION OF POSITION-SKIN BLOCKS AMONG DIFFERENT FISH OIL FATLIQUORS

SKINS	POSITION					
	B	D	A	F	C	E
2	I	II	III	IV	V	VI
6	II	III	IV	V	VI	I
3	III	IV	V	VI	I	II
4	IV	V	VI	I	II	III
1	V	VI	I	II	III	IV
5	VI	I	II	III	IV	V

The six blocks from the six skins for each experiment were distributed among six oils to produce the Latin-square design shown in Table V. At the top of the table are given the block-position letters selected at random. The six skin numbers selected at random are given on the left side of the table. The Roman numerals I to VI in the Latin square represent the six oils used in fatliquoring the leather samples in an experiment. The oils were assigned

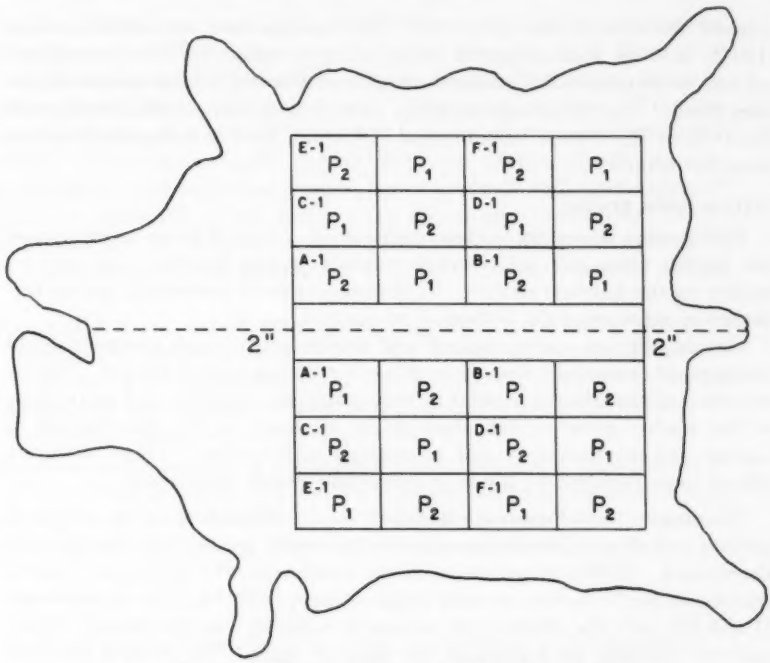

FIGURE 1.—Sampling of chrome-tanned kipskins in the blue.

Number of 14″ × 4″ blocks cut from each side—6. Blocks designated by letters.

Number of skins—6. Skins designated by number following letter.

Each block was split into halves and divided as shown above between process-1 oils and process-2 oils.

the Roman numerals at random. The block samples from the six skins then were distributed among the six oils by associating the Roman numeral in a block with its row-skin number and column-position number. Since mated positions from each side of the skins were taken, there was a total of 12 blocks for each oil.

These 12 blocks were cut in half and divided in a crisscross manner between sulfation process 1 and sulfation process 2, as shown in Fig. 1. This constituted the split-plot design of the experiment intended to show differences between leathers fatliquored with sulfated oils prepared by two processes.

Fatliquoring procedure.—The fatliquoring procedure consisted in milling leather samples in twice their weight of water for 15 min. and then neutralizing with 1% sodium bicarbonate solution on the wet basis of the chrome-

tanned stock for 30 min. at 120°F. The samples then were fatliquored at 120°F. in twice their weight of liquor, using a mixture of 60 parts sulfated oil and 40 parts raw oil, to allow the leather to absorb 6% of oil on a moisture-free basis. The fatliquored samples, after drying, were conditioned for 48 hr. at 50 ± 5% relative humidity and 72° ± 1.8°F. The fatliquored leathers were not staked.

Extractable grease

Fatliquoring allows the leather to absorb oil. This oil forms a film around the leather fibers and reduces their cohesion, giving flexibility and serviceability to the finished product. A determination of extractable grease furnishes an estimate of the amount of oil present.

Certain oils are easily oxidized and polymerized. Such reactions could produce an excessively firm piece of leather having a hard surface. Determination of the relative amount of extractable grease before and after aging of the leather gives an indication of the tendency of the absorbed oil to oxidize and polymerize as well as combine with leather. These combined effects were measured by a loss in extractable grease upon aging.

Procedure.—In fatliquoring experiment I, the effect both of the sulfation process and of aging on the amount of extractable grease in the leather was determined. In the aging portion of the experiment, the fatliquored leather was stored for 9 months at room temperature. In fatliquoring experiments II and III, only the effect of the process of sulfation was determined. Time was not available for a study of the effect of aging. The method used for determining the amount of extractable grease was that of the American Leather Chemists Association (3).

TABLE VI

EFFECT OF PROCESS OF SULFATION AND OF AGING ON EXTRACTABLE GREASE IN LEATHERS FATLIQUORED IN EXPERIMENT I

Kind of Oil	Iodine No. of Raw Oil	Sulfation Process	Amount of Extractable Grease (on dry-weight basis)		
			Before Aging %	After Aging %	Decrease Due to Aging (relative %)
Ocean perch	119	1	6.13	5.52	10.0
	119	2	6.33	5.99	5.4
Herring	131	1	6.19	5.60	10.5
	131	2	6.44	6.01	6.7
Herring	139	1	6.68	5.53	17.2
	139	2	6.40	5.65	11.7
Salmon	166	1	5.74	5.19	9.6
	166	2	5.84	5.13	12.2
Menhaden	152	1	6.06	5.09	16.0
	152	2	6.18	5.26	14.9
Menhaden	176	1	6.41	4.67	27.1
	176	2	6.06	4.92	18.8

Note: The aged leathers were stored for 9 months at room temperature.

Results.—The data on amount of extractable grease obtained in experiment I are given in Table VI. The data show that the amount is about 6%. The amount of extractable grease before aging did not differ greatly between sulfation process 1 and sulfation process 2. After aging, however, all the oils except salmon showed a greater decrease in amount of extractable grease for process 1. Thus, the sulfation process involving dilution of sulfuric acid with phosphoric acid tended to produce less breakdown and combination of the fatliquor absorbed by the leather. In the present experiment (I) the more unsaturated of the two menhaden oils showed the greater effect of aging, with the effect being considerably greater for process 1 than for process 2.

In an earlier study, cod oil, which presently is used in the leather industry, was found to be similar to menhaden in the amount of extractable grease. The conclusion from the present study thus is that ocean perch oil, herring oil, and salmon oil fatliquors as used in this study do not show undesirable decreases in the amount of extractable grease.

The data on the amount of extractable grease obtained in experiments II and III are given in Tables VII and VIII, respectively. In agreement with experiment I, no great differences were found in the amount of extractable grease in the non-aged leather as a result of the process of sulfation used.

TABLE VII

EFFECT OF PROCESS OF SULFATION ON EXTRACTABLE GREASE IN LEATHERS FATLIQUORED IN EXPERIMENT II

Kind of Oil	Iodine No. of Raw Oil	Sulfation Process	Extractable Grease in Non-aged Leather (on dry-weight basis) %
Ocean perch	119	2	5.79
	119	3	5.81
Herring	131	2	5.84
	131	3	6.04
Salmon	166	2	5.95
	166	3	5.89
Menhaden	152	2	5.45
	152	3	5.51
Menhaden	176	2	5.55
	176	3	5.45
Cod	176	2	6.26
	176	3	5.93

Firmness

Both firmness and surface hardness were considered important because they give information to the tanner regarding the temper and feel of the leather.

TABLE VIII

EFFECT OF PROCESS OF SULFATION ON EXTRACTABLE GREASE IN LEATHERS FATLIQUORED IN EXPERIMENT III

Kind of Oil	Iodine No.	Sulfation	Extractable Grease in Non-aged Leather (on dry-weight basis) %
Ocean perch	119	1	5.77
	119	4	5.73
Herring	131	1	5.53
	131	4	5.51
Salmon	166	1	5.48
	166	4	5.32
Menhaden	152	1	5.47
	152	4	5.12
Menhaden	176	1	5.47
	176	4	5.49
Cod	176	1	6.09
	176	4	5.82

Procedure.—The firmness was determined by cutting 1″ x 4″ leather samples, rolling them into hollow cylinders 1″ in diameter, and measuring the force required to compress the cylinders by means of a Schiefer compressometer. This instrument consists of a foot which is 1″ in diameter, the movement of which is recorded in thousandths of an inch. The force exerted against the foot also is indicated. In the present test, the reading taken was the force exerted when the cylinder was compressed ½″.

Results.—Lack of space precludes the presentation of all the data collected. An example of the way in which the compressometer values collected in fatliquoring experiment I were analyzed is given in Table IX. To understand the table refer to Fig. 1. Note the block A-1 on the right side of the skin, and note the sub-block A-1P_r. Now note the corresponding sub-block A-1P_l on the left side of the skin. Compressometer values were taken on these two sub-blocks and added together. In the case of ocean perch oil, this gave the value 32 appearing in Part A of Table IX, corresponding to process 1 and position A. Thus the actual compressometer readings are half the magnitude shown in the table.

To understand Part B of the table, refer to "ocean perch" in Part A and position A. Now add 32 and 35 for processes 1 and 2 to get the sum of 67. This value of 67 is shown in Part B under "ocean perch" for skin 5.

The other values for Parts A and B were derived similarly. These then were used in the analysis of variance shown in Part C, which was computed as described by Cockran and Cox (1).

TABLE IX

COMPRESSOMETER DATA FOR AGED LEATHER SAMPLES IN FATLIQUORING EXPERIMENT I

Part A—Subposition Sums

Position	Ocean Perch Oil I_2 No. = 119		Herring Oil I_2 No. = 131		Salmon Oil I_2 No. = 166		Herring Oil I_2 No. = 139		Menhaden Oil I_2 No. = 152		Menhaden Oil I_2 No. = 176	
	Process 1	2	1	2	1	2	1	2	1	2	1	2
A	32	35	38	29	32	27	28	28	30	33	32	40
B	20	26	30	24	36	24	23	32	35	31	31	40
C	30	32	34	23	29	36	27	32	36	35	26	36
D	33	35	24	19	28	30	25	30	31	36	35	35
E	28	32	29	26	39	41	25	28	31	41	29	34
F	24	31	39	32	23	23	20	31	34	39	31	32

Part B—Process Sums

Skin	Ocean Perch Oil	Herring Oil	Salmon Oil	Herring Oil	Menhaden Oil	Menhaden Oil
1	55	57	60	53	63	70
2	68	67	65	51	66	63
3	60	54	59	55	71	73
4	62	55	58	55	73	72
5	67	71	80	59	67	71
6	46	43	46	56	72	62

Part C—Analysis of Variance

Source of Variation between	Degrees of Freedom	Sum of Squares	Mean Sum of Squares	$F_{\alpha=0.05}$
Oils	6-1 = 5	423	84.60	4.63
Skins	6-1 = 5	365	73.00	4.00
Positions	6-1 = 5	107	21.40	1.17
Error—A	(6-1)(6-2) = 20	365	18.25	
Between Sulfation process (Oil Sulfation Processes)	2-1 = 1	52	52.00	5.43
	(1)(5) = 5	348	69.60	7.27
Error—B	(6)(5)(1) = 30	287	9.57	
Total	(6)(6)(2)-1 = 71			

The analysis of variance failed to indicate that the sulfated oils prepared by different processes within an experiment and used to fatliquor leather within an experiment produced significant differences in leather firmness. Hence, within an experiment, the data obtained on the different methods of sulfation with a given oil could be combined. The results are given in Table X. A specific example will show the method of computing the data. The value 14.9 for aged leather fatliquored with ocean perch oil in fatliquoring

TABLE X

MEAN COMPRESSOMETER READINGS

Fatliquoring Oil	Iodine No. of Raw Oil	Fatliquoring Experiment I		Fatliquoring Experiment II	Fatliquoring Experiment III
		Non-aged Leather	Aged Leather	Non-aged Leather	Non-aged Leather
Ocean perch	119	15.9	14.9	15.7	19.4
Herring	131	17.7	14.4	15.7	19.2
Herring	139	17.6	13.7	—	—
Salmon	166	21.6	15.3	17.6	21.5
Menhaden	152	20.9	17.2	—	—
Menhaden	176	20.6	16.7	17.8	20.5
Menhaden	176	—	—	16.9	19.1
Cod	176	—	—	16.9	18.7

experiment I, for example, was obtained by adding 55, 68, 60, 62, 67, and 46 shown under "ocean perch" in Part B of Table IX and dividing the sum by 24. This value of 24, in turn, was obtained as the product of 2 subpositions $\times$ 2 sulfation processes $\times$ 6 skins. Hence, the value 14.9 shows the actual magnitude of the compressometer reading. Within an experiment there were significant differences between compressometer readings for the various oils. However, on the basis that cod oil and menhaden oil fatliquors as used in this and past studies do not produce leather that is too firm, the results in Table X failed to indicate that perch oil, herring oil, and salmon oil fatliquors produced leathers which were more firm than leathers fatliquored with cod oil and menhaden oil.

Surface hardness.—The surface hardness measurement was used to indicate if the polymerization properties of any of the fish oils produced an excessively hard surface. The experiments were designed to show whether or not ocean perch oil, herring oil, and salmon oil fatliquors produced a harder surface on leather than did cod oil or menhaden oil fatliquors.

Procedure.—Surface hardness was measured with the Trionic rubber hardness gauge in Shore units.

Results.—Statistical analysis of the data failed to indicate that sulfated oils prepared by different processes within an experiment and used to fatliquor leather within an experiment produced significant differences in the hardness of the surface of leather. The data on processing therefore were combined, and the mean values for surface hardness are reported in Table XI. The values were computed in the same manner as in Table X. Statistical analysis of the raw surface hardness data for each experiment indicated that significant differences in surface hardness existed between fatliquored leathers for experiments I, II, and III.

TABLE XI

MEAN SURFACE HARDNESS READINGS

Fatliquoring Oil	Iodine No. of Raw Oil	Fatliquoring Experiment I		Fatliquoring Experiment II	Fatliquoring Experiment III
		Non-aged Leather	Aged Leather	Non-aged Leather	Non-aged Leather
Ocean perch	119	65.1	76.7	76.1	76.5
Herring	131	66.1	75.1	77.6	75.7
Herring	139	67.8	76.6	—	—
Salmon	166	68.8	76.0	77.1	78.8
Menhaden	152	65.4	77.3	—	—
Menhaden	176	67.2	78.8	80.1	79.6
Menhaden	176	—	—	78.7	79.2
Cod	176	—	—	74.4	72.4

The data in Table XI for the three experiments fail to replicate and conclusively prove differences in fatliquors from the oils of ocean perch, herring, salmon, and menhaden. The data do indicate, however, that cod oil-fatliquored leather has a lower surface hardness than has any of the other fatliquored leathers.

Under similar conditions leather fatliquored in the past both in the laboratory and in the pilot plant failed to indicate differences in surface hardness between leathers fatliquored with cod oil and menhaden oil. Therefore, under the conditions that these and past fatliquoring experiments were performed, no definite conclusions can be made at the present time regarding differences in surface hardness properties between leathers fatliquored with oils of perch, herring, salmon, menhaden, and cod. Apparently if differences in surface hardness do exist, they are not great.

Yellowing.—For certain uses the yellowing of leather surfaces makes the product less desirable, for example, in the manufacture of white or pastel leathers. Determination of whether or not a fatliquor causes leather to yellow therefore is of interest.

Procedure.—Factors influencing the yellowing of leather are light, temperature, relative humidity, and time. The test conditions for studying yellowing of leather surfaces, therefore, were (*a*) exposure of samples under a R-A type General Electric Sunlamp for 72 hr. at a surface temperature of 150° ± 5°F., (*b*) exposure of samples in a closed oven for 1 week at 120° ± 5°F. and at a relative humidity of 95%, and (*c*) exposure of samples under the same conditions as in (*b*) except that the relative humidity was changed to 17%.

Results.—All fish oils under all test conditions produced yellowing of leather surfaces. The test conditions resulting in the greatest degree of yellowing were 1 week at 120° ± 5°F. and 95% relative humidity.

Gummy spew

Procedure.—The samples were examined under a stereoscopic microscope for gummy spew.

Results.—None of the fish oils produced spew on leather.

SUMMARY

At present cod oil is the only fish oil used extensively in the leather industry. The purpose of the present series of studies was to determine if the oils of ocean perch, herring, salmon, and menhaden also could be used, particularly in fatliquoring. Earlier studies had indicated that menhaden oil was suitable for such usage. The purpose of the present paper was to study the suitability of the other oils.

The quality factors considered in the present study were: amount of extractable grease, firmness, surface hardness, yellowing, and gummy spew. Since the industry already uses cod oil and since earlier tests had indicated that menhaden oil produces a leather with properties similar to that produced by cod oil, leathers fatliquored with menhaden oil and cod oil were used as the basis for comparing the leathers fatliquored by the oils of ocean perch, herring, and salmon.

The amount of extractable grease was not significantly related to the kind of oil used or the process used to sulfate the oil, nor was the decrease in the amount, upon aging, so related. The relative percent decrease in extractable grease from leather upon aging was the greatest for menhaden oil–fatliquored leather as compared to leathers fatliquored with ocean perch oil, herring oil and salmon oil. In an earlier study cod oil–fatliquored leather was found to be similar to menhaden oil–fatliquored leather regarding percent extractable grease upon aging. Use of sulfated oils prepared from the sulfation process involving dilution of sulfuric acid with phosphoric acid tended to decrease the relative percent decrease of extractable grease from

leather upon aging. The firmness of the leather was not significantly related to the process used to sulfate the oil, and compared to cod oil none of the fish oils produced a firmer leather. The data indicated that the surface hardness also was not related to the process of sulfation, but there was evidence that the surface of leather fatliquored with the oils of ocean perch, herring, salmon, and menhaden was harder than was that of leather fatliquored with cod oil. (Additional study would be required, however, to establish unequivocally whether a difference in surface hardness actually exists.) All the fish oils studied produced yellowing of leather surfaces. None produced gummy spew. The tentative conclusion pending clarification of the question of surface hardness is that, regardless of the method of sulfation used, ocean perch, herring, salmon, and menhaden oil will produce fatliquored leather with properties similar to those of leather fatliquored by cod oil.

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The educational values in the study of science go far beyond the practical matters of a cold technological war or even those of the wise use of science in the service of society. The student of science quickly learns that all scholars seek the truth and that they must be critical and honest with each other. The study of science may offer to the young student his first and possibly his best early opportunity for learning how easy it is to make mistakes and how hard it is to advance knowledge. It may also provide the simplest early experience of the supreme virtue of intellectual honesty.

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—*Education for the Age of Science*, President's Science Advisory Committee, 1959.

LIFE LINES

Brief Biographies of Our Contributors

CLARENCE W. BEEBE, a graduate of the University of California, is Supervisor of the Tanning Materials Unit, Eastern Regional Research Laboratory, U. S. Dept. of Agriculture, where he has been employed for some thirty years.

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VICTOR MATTEI—See the October, 1959, *Journal.*

DR. JOSEPH NAGHSKI—See the April, 1959, *Journal.*

WILLIAM T. RODDY—See the October, 1959, *Journal.*

DR. D. G. ROUX graduated from the University of South Africa in 1945 with an M. Sc. degree (distinction) for his work on essential oils of rutaceous plants. After a brief period as research chemist for the United Tobacco Company, Cape Town, he joined the staff of the Leather Industries Research Institute, Grahamstown, in 1947, where at present he holds the post of Senior Research Officer. Dr. Roux has specialized in the chemistry of wattle tannins and has published works on tannins, catechins, and anthocyanidins in British, German, and American chemical and leather literature. He received the Donald Burton Prize (1950), the Ph.D. degree of Rhodes University (1952), and the Fellowship of the Royal Institute of Chemistry (1955). During 1954, on a travel grant from the Leather Institute, he studied catechin chemistry with Professor Karl Freudenberg at the Chemical Institute, Heidelberg University, Germany, and chromatography at the Low Temperature Research Station, Cambridge, England.

DR. WALLACE WINDUS is Editor-in-Chief of *JALCA*. For further biographical data, see the March, 1959, *Journal.*

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1960—Lake Placid Club, Lake Placid, New York, June 19–22

1961—Haddon Hall Hotel, Atlantic City, New Jersey, June 11–14

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ABSTRACTS

Studies of the Improvement of Rawhide Quality. Dr. Ch. Gastellu, I. Jullien, J. Prevot, and A. M. Ginisty. *Bulletin de l'Association Française des Chimistes des Industries du Cuir*, **21**, 16–23 (1959).—**I.** This study consisted of (*a*) comparative experiments in salting with the purpose of finding the best conditions for the preservation of skins and (*b*) a study in the microbiology laboratory to elucidate the cause of defects occurring in preservation. The salting experiments comprised 336 calfskins divided into lots. The object was to verify the previous observations concerning the influence of refrigeration, the addition of sodium carbonate and naphthalene, and the influence of the elimination of constituents of the skin (albumins, globulins, lipids) which can serve as culture medium. Results indicate the following: (1) The defects most characteristic were punctures on the flesh side and round stains on the grain side. (2) The round stains were extremely numerous on the control experiment salted and stored at ambient temperature. (3) The salting with additional sodium carbonate and naphthalene assured in all cases the best preservation. However, in cases where the skins were previously washed, fleshed, and stocked in the cold even for only 15 days, they were free of all defects. (4) In the absence of carbonate and naphthalene, washing and fleshing the skins improved them. The salting of skins previously cooled and stocked in the cold attenuated the number and importance of round stains.

II. This study had for object the separation and characterization of microorganisms responsible for red colorations and violet spots and finding a convenient culture medium. From many culture media that of Bussault and LaChange was retained for red colorations. The bacterium responsible for red colorations was isolated and identified in all its forms. The isolation and characterization of the bacteria causing violet spots was not successful, and this work is now in progress.

III. Research against bovine hypodermose. Note by Dr. Magat. The following is a résumé of studies conducted during the year 1958 for new procedures of preventive treatment against bovine hypodermose. (1) Dusting of insecticide on cattle during the summer of 1957 with an emulsion of lindane consisting of 1.3 g/l did not give satisfactory results. (2) Early and external treatment consists of the insecticide Bayer L 13/59 in oily emulsion having high cutaneous penetration. This treatment was applied on a large scale at the beginning of 1958 and was favorable. (3) The first season of experimentation with the internal treatment has brought out the activity of the American product Dow ET 57. The satisfactory results on 9 heads of cattle confirmed recent American and English publications. R.H.

Fabrication of Split Chrome Leather for Heat-resistant Gloves. Dr. Ch. Gastellu and I. Jullien. *Bulletin de l'Association Française des Chimistes des Industries du Cuir*, **21**, 23–25 (1959).—Six different compositions consisting of fish oil, mineral oil, Moellon, and kaolin for the fatliquoring of leather were applied to split butts of cattle after chrome tanning according to usual procedures. The resistance to heat was as follows: (1) Leathers heated for 5 min. at 300°C. were very much affected; the leather was retracted, hard, and carbonized. Comparisons at this temperature were only possible for a

1-min. duration. (2) Leathers with no mineral charge had a surface retraction of 35%, while those with a mineral charge had a 25% retraction. (3) The nature of the oil does not have any influence on the behavior of leather toward heat. (4) The texture of the leather has a certain importance in its behavior toward heat. Parts taken from the loose portion of the hide resist heat at 300°C. better than parts taken from the firm and compact region. R.H.

Adsorption of Negatively Charged Complexes by Cation Exchangers. K. A. Kraus, D. C. Michelson, and F. Nelson. *J. Am. Chem. Soc.*, **81**, 3204–7 (1959).—Strong adsorption of some negatively charged chloride complexes of Au and Fe by the cationic exchange resin Dowex 50 is demonstrated. This adsorption is negligible at low ionic strength, increases rapidly with ionic strength, and is much greater from salt solutions than from acid solutions. The adsorption is strongly dependent on the type of complex. H.B.M.

Contraction of a Gelatin-Water System. H. Hirano. *Nippon Suisangaku Kaishi.*, **24**, 330–33 (1958–59); *Chem. Abstr.*, **53**, 11464*b*.

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N- and C-Terminal End Groups of Hair Keratin. M. F. Kerr and C. Godin. *Can. J. Chem.*, **37**, 11–12 (1959); *Chem. Abstr.*, **53**, 12378*e*.

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Chromium Loss in Combination Tanning of Sole Leather. I. Feher and I. Kerese. *Bör-es Cipotech.*, **8**, 151–54 (1958); *Chem. Abstr.*, **53**, 12721*a*.

Making Footwear Upper Leather Materials Water-repellent with Organosilicon Compounds. E. K. Maminov. *Khim. i. Primenenie Kremneorg. Soedienenii, Trudy Konf. Leningrad*, **1958**, No. 4, 65–72; *Chem. Abstr.*, **53**, 12722*a*.

Protective Effect of Sulfates on Collagen. N. I. Egorkin and L. G. Kazhdan. *Trudy Leinigrad. Tekhnol. Inst. im. Lensoveta*, **30**, 106–10 (1954); *Chem. Abstr.*, **53**, 12722*f*.

Occurrence of "Esterlike" Linkages in Collagen. P. M. Gallop, S. Seifter, and E. Meilman. *Nature*, **183**, 1659–61 (1959).—Three types of gelatin (commercial acid- and base-processed gelatins and gelatins prepared from calfskin and carp swim-bladder procollagens) were treated with hydroxylamine under conditions favoring the disruption of ester bonds. A fast and a slow

reaction, each characterized by the formation of protein-bound hydroxamide, occurred. The fast reaction results in a decrease in molecular weight of the original protein to a protein of about 20,000 molecular weight, with no increase in free amino groups to indicate the splitting of peptide bonds. These results indicate the presence of esterlike (or perhaps imide) linkages between units or chains of about 20,000 molecular weight; these chains are joined together in parent gelatin. Similar preliminary results have been obtained with hydrazine. C.D.

Infrared Study of Oxidized Keratin. H. H. Stein and J. Guarnaccio. *Textile Research J.*, **29,** 492–6 (1959).—The infrared spectrum of oxidized human hair, callus, or wool shows a characteristic absorption band at 9.6 μ, possibly due to the presence of a sulfoxide group. C.D.

Interpretation of Fiber Properties. I. Role of Single Fiber Flex Fatigue in Abrasion Resistance of Fabrics. T. B. Lefferdink and H. P. Briar. *Textile Research J.*, **29,** 477–82 (1959).—An investigation was made of the resistance of single fibers to attrition by various types of physical processes. For widely different types of fibers (wool, cotton, glass, nylon, etc.) only one of these processes, the rate of fracture caused by fatigue on repeated bending of single fibers, had any significant degree of correlation with the rate of their destruction in fabrics during actual wear tests. The relative resistance of the fiber types to fatigue varies with the severity of the bending process, a fact which explains the lack of correlation of any single fabric abrasion test with actual performance in all but a narrow field of application. A relatively simple test was developed to measure the resistance of single fibers to fatigue in flexure. When they were flexed over a rounded metal bar, the log of the number of flexures to failure is approximately linearly related to the radius of curvature of the surface of the bar and to the tension on the fiber during the test. Results of these tests seem to indicate that the predominating mechanism of attrition due to rubbing and other physical processes in many if not most apparel applications is that of fracture of the fibers due to fatigue in flexure. C.D.

Frictional Measurements on Fibrous Materials. W. F. duBois. *Textile Research J.*, **29,** 451–66 (1959).—A method for measuring the coefficient of static friction for fibrous material is described, and results for wool and other materials are tabulated. A statistical analysis of the relationship between frictional force, W, and normal load, N, does not confirm the empirical equations of other workers but leads to the formula: $W = A_1 + A_2 N + A_3 N^2$, where A_1, A_2, and A_3 are constant for a given material. C.D.

Acrylonitrile-Stabilized Wool Keratin Derivatives. Y. Tomimatsu, J. J. Bartulovich, and W. H. Ward. *Textile Research J.*, **29,** 593–4 (1959).—Data are presented on the physical properties (for example, molecular weight as determined by ultracentrifuge and by light-scattering studies) of a cortical cell protein preparation from merino wool made water-soluble by reduction with mercaptoethanol and stabilized by acrylonitrile. C.D.

Isolation and Identification of Urocanic Acid Found in Extracts of Raw Wool. C. H. Binkley and F. T. Jones. *Textile Research J.*, **29,** 574–77 (1959).—Urocanic acid in 2 isomeric forms is present in the H_2O extract of raw wool. It causes discoloration of wool at 55°C. and high humidity. C.D.

Some Mechanical Properties of Single Wool Fibers in D_2O. M. Feughelman, A. R. Haly, and T. W. Mitchell. *Textile Research J.*, **29,** 564–67 (1959).—Load-extension and stress-relaxation curves of wool fibers in H_2O and in D_2O and the rates of penetration of H_2O and of D_2O fronts into dry wool fibers were determined. In all cases D_2O acts in the wool in the same manner as H_2O at a temperature reduced by about 5°–6°. These facts are in agreement with the concept that in the diffusion of water and also in stress-relaxation and extension in the yield region, formation and breaking of hydrogen bonds occur. C.D.

Kinetic Study of the Supercontraction of Wool Fibers in Solutions of Salts, Acids, and Alkalies. W. G. Crewther and L. M. Dowling. *Textile Research J.*, **29,** 541–49 (1959).—Wool fibers contract in hot solutions of acids and alkalies, the initial rate of contraction increasing with increasing concentration. At the higher concentrations, contraction is followed by elongation to lengths which may exceed the original length. Kinetic curves for the contraction of wool fibers in *N* HCl-containing salts show well-defined two-stage contraction. With 5 or 6*M* LiI or 6*M* NaI the fibers contract by about 25%, elongate to a length which may approach the original, and again contract; in such solutions a considerable proportion of the wool protein is dissolved and a S-rich residue is left. The two-stage contraction kinetics are interpreted in terms of the contraction at different rates of two structures in the wool fiber. C.D.

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Tryptophane Content of Weathered Wool and Mohair and Morphologically Deviating Wool. D. P. Veldsman. *Chem. and Industry*, **1959,** No. 27, 878–80.—Tryptophane contents are listed of a number of samples of root portions and of weathered tip portions of merino wools and of mohair, and of the root and middle portions of wool from Cu- and from Co-deficient sheep. C.D.

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Elongation of Rat Tail Tendon on Hydration. H. R. Elden.. *Nature*, **183**, 1681–82 (1959).—The rate and extent of elongation of dry rat tail tendon in H_2O and in aqueous solutions of various alcohols are tabulated. C.D.

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Chestnut Wood—Basic Data for Estimating Its Technological Value. F. V. Gaio. *Estud. e Inform. Direc.-geral serv. florestias e aquicolas* (Portugal), **No. 65-D3**, 7 pp. (1956); *Chem. Abstr.*, **53**, 13583*i*.

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Studies on the Enzyme Depilation of Hides and Skins. VI. Unhairing of Goatskin with Protease Produced by *Bacillus Megatherium* 3E. H. Toyoda and A. Futami. *Bull. Japanese Assoc. Leather Technol.*, **5**, 61–69 (1959) (English summary).—The enzyme obtained from culture filtrates of *B. megatherium* by extraction, precipitation with $(NH_4)_2SO_4$, dialysis, and precipitation with acetone, had high proteolytic activity but contained no amylase, invertase, maltase, lactase, cellulase, hyaluronidase, or pectase. Progress of depilation of goatskin by this enzyme was followed by measuring depilation load. There was always an initial lag period, followed by a period in which the degree of hair loosening increased rapidly, and finally a period of slower increase in loosening. The length of the lag period varied with conditions. When the skin pieces were left in the enzyme for "some time", the epidermis was detached in sheets, bringing the hair with it. Rate of depilation increased with enzyme concentration (almost complete in 6 hr. at 30°C. with 0.04% enzyme), was maximum at pH 7 (effective at 6 to 8), and was maximum at 30°C. for 0.01% enzyme but at 35°–40°C. for 0.02% enzyme. Activity was accelerated slightly by NH_4Cl, $CaCl_2$, and $CaSO_4$; inhibited by $HgCl_2$, $KMnO_4$ and EDTA; unaffected by ascorbic acid, cysteine, and CH_2ICOOH. Unhairing was accelerated by soaking with alkalies (Na_2CO_3, Na_2S, $Ca(OH)_2$), retarded by soaking with acids, and unaffected by soaking with NaCl or urea. H.B.M.

Application of Ion-Exchange Membrane in Vegetable Tanning. E. Sugano and I. Nishiyama. *Bull. Japanese Assoc. Leather Technol.*, **5**, 71–74 (1959) (English summary).—Vegetable tan liquor was electrodialyzed using Amberplex C-1 membrane to lower the pH by converting salts into organic acids. Tannin content did not change. No differences could be detected between leathers tanned in the dialyzed liquor and in liquor brought to the same pH by adding organic acid. The authors think that the original salt content, which was changed to acid by dialysis, was too small to matter. H.B.M.

Studies on the Stripping of Vegetable Tannins from Leather. I. Alkali, Acetone, and Urea Extraction of Vegetable-tanned Hide Powder. Y. Sakimoto and N. Kurakata. *Bull. Japanese Assoc. Leather Technol.*, **5**, 75–80 (1959).—Hide powders, tanned with chestnut or soluble quebracho, from which water solubles had been removed, were extracted with Na_2CO_3, 50%

aqueous acetone, or urea solution. In extracting with Na_2CO_3, no relationship was found between dissolved collagen and extracted tannin. The acid-combining power of the powder was not affected by stripping with urea but increased after stripping with 50% acetone. The authors say that the amounts of tannin extracted corresponded to the degree of solubility of the tannin in the extractant. Resistance to stripping increased as the leather was aged—more by dry than by wet aging—and was accompanied by a decrease in acid-binding power. H.B.M.

Studies on Leather for Gas Diaphragms. II. The Mutual Reaction of Coal Gas–Oil–Leather Systems. M. Kubota. *Bull. Japanese Assoc. Leather Technol.*, **5**, 81–87 (1959) (English summary).—Diaphragm is either Cr-tanned (about 1% Cr_2O_3) or vegetable-tanned (degree of tannage 45–60), and in either case contains 50–60% fat. Deterioration manifests itself by loss of oil, hardening, and leaking. Failed diaphragms showed a drop in strength, a decrease in oil content, an increase in degree of tannage, and an increase in acid value and a decrease in iodine value of the oil. Of coal tar components investigated, only pyridine weakened the leather. When coal gas was passed through the oil, acid value increased, and iodine value decreased only slightly. The color darkened. When cod leather oil was used, the dark-colored component was taken up by the leather, and the degree of tannage increased. When diaphragm leather was immersed in the oil through which gas was blown, the shrink temperature declined slightly, but degree of tannage was unchanged unless cod oil was used. H.B.M.

The Amino Acid Composition and Morphology of Some Invertebrate and Vertebrate Collagens. K. Piez and J. Gross. *Biochim. et Biophys. Acta*, **34**, 24–39 (1959).—The complete amino acid analysis (column chromatography according to Moore and Stein) of collagens from a mammal (steerhide), an elasmobranch (shark elastoidin), an echinoderm ("Thyone" body wall), and two coelenterates ("Metridium" body wall and "Physalia" float), and that of two structurally distinct collagens from the sponge are presented along with a description of some morphological characteristics of the tissues from which they were derived. The glycine content of the collagens was very uniform, ranging from 306 to 334 residues per 1,000. There are no striking features in the amino acid composition of invertebrate collagens which distinguish them from vertebrate collagens. The invertebrate collagens have a smaller proportion of imino acids (particularly proline), a larger content of hydroxyl groups (owing largely to threonine and serine), uniformly higher amounts of hydroxylysine, a greater proportion of dicarboxylic acids, and fewer nonpolar amino acids. There appears to be no obvious relationship between amino acid composition and evolutionary level. J.M.C.

The Specificity of Collagenase. Y. Nagai and H. Noda. *Biochim. et Biophys. Acta*, **34**, 298–99 (1959).—A series of synthetic peptides were investigated as substrates for collagenase. From poly (Pro. Leu. Gly) of average molecular weight 3000, collagenase liberates three peptides with the amino acid sequence Pro. Leu. Gly. Pro. Leu. Gly. Pro. Leu, and Gly. Pro. Leu. Gly. respectively. No glycine or Pro. Leu. was found among the digestion products. Incubation of Gly. Pro. Leu. Gly. Pro. NH_2 with purified collagenase gave two peptides with amino acid sequences Gly. Pro. Leu. and Gly. Pro. NH_2 and no free amino acids. It is concluded that the sequence Pro. R. R'. Pro. is necessary in a substrate for collagenase. J.M.C.

A New Method for Isolation of Hydroxy-L-Proline and L-Proline from Gelatin. M. Levine. *J. Biol. Chem.*, **234**, 1731–32 (1959).—A gelatin hydrolyzate is treated with nitrous acid to destroy all α-amino acids. L-proline and hydroxy-L-proline are regenerated by hydrolysis of their nitrosamines with 6*N* HCl. After extraction of ether-soluble materials and vacuum distillation to remove HCl, 9.5 g. of proline and 9.4 g. of hydroxyproline per 100 g. of gelatin were found by colorimetric analysis. The imino acids were separated on a Dowex-50 column by gradient elution with dilute HCl. Further purification of the two fractions, the concluding step being crystallization, resulted in yields of 6 g. uncontaminated L-proline and 5.7 g. uncontaminated hydroxy-L-proline per 100 g. gelatin. J.M.C.

Proline Iminopeptidase. S. Sarid, A. Berger, and E. Katchalski. *J. Biol. Chem.*, **234**, 1740–46 (1959).—A newly prepared enzyme which acts on peptides of high molecular weight as a specific exopeptidase, cleaving N-terminal L-proline residues exclusively, produced no proline, hydroxyproline, or any other amino acid from gelatin. J.M.C.

***Aspergillus*, *Penicillium*, and *Paecilomyces* Occurring in the Tannery.** J. M. Adzet. *Bull. Assoc. Franc. Chim. Ind. Cuir*, **21**, 79–96 (1959).—Some molds were isolated from liquid extracts and fresh plumping liquors; others, from split leathers and spent liquors. Among 41 isolated strains 12 different species were obtained, as follows: *Aspergillus niger*, *A. flavus*, *A. unguis*, *A. terreus*, *Penicillium frequentans*, *P. chrysogenum*, *P. notatum*, *P. cyclopium*, *P. diversum*, *P. variable*, *Paecilomyces varioti*, and *Goetrichum candium*. In order to determine if the isolated strains constituted a flora capable of growing on tannin solutions, the strains were placed on tannin solutions of different concentrations. Solution I consisted of tannin from gall nuts, solutions II through IV of chestnut extract, and solution VII was composed of nontannins obtained in part from chestnut extract. In most cases starting from the fifth day the solutions of chestnut extract deposited a crystalline precipitate which was identified as ellagic acid. The development of the strains was generally slight on solutions of tannin from gall nuts, a little stronger on solutions of nontannin, and abundant on solutions of chestnut extract. Most of the solutions of gall tannin were decolorized, and electrophoresis determinations of the solutions indicated that the tannin disappeared or was grealty diminished. Gallic acid increased, or hydrolysis took place. The non-decolorized solutions gave an electrogram resembling the control. In order to obtain more information about strains and their possible action in the tannery, their growth on a solid tannin medium and their action on a few proteins (skin, gelatin, casein) and on starch were studied. A medium consisting of the extract of chestnut solidified with agar was prepared. This medium permitted the growth of molds but did not allow yeast and bacteria to grow. It has the advantage over the usual laboratory medium in being closer to the natural medium of these molds in the tannery, thus preserving the normal aptitude of the strains. Only *Aspergillus flavus*, *A. terreus*, and *Penicillium notatum* hydrolyzed gelatin strongly. A microscopic examination of the skins prepared for tannage indicated no damage. Three strains of *Penicillium frequentans* produced under the conditions of the experiments a pigment which colored the skins brown. Starch is hydrolyzed by all the molds and casein only by certain ones. R.L.H.

The Best Conditions for Preserving Leather and Raw Stock. M. Riviere. *Bull. Assoc. Franc. Chim. Ind. Cuir*, **21**, 44–51 (1959.)—The methods of hide preservation in Europe and the Americas are reviewed. In Australia the treatment of raw stock conforms to that of the Americas in many ways, but the shipment of calfskins merits an explanation. The calfskins are placed in wooden casks hermetically sealed, leave Australia in summer, pass through the tropics at 40°C., and arrive in Europe in the spring (2-month period) without undergoing damage. The hide of a light calf slaughtered in Strasbourg in January, 1958, (temp. –10° C.) was washed and immediately cut into discs 20 cm. in diameter. The discs were weighed and numbered according to a determined order and were placed in a sealed glass cylinder with the exterior blackened to filter off light. The discs were separated by a layer of marine salt and placed from bottom to top in a predetermined order. The cylinder was then placed in a refrigerator at 6° C. in January, 1958. Every three months a disc is removed and submitted to analytical measurements made in the same way. No trace of degradation has been detected. In a second experiment 800 kg. of calfhides from calves slaughtered October 7 were obtaind in Strasbourg and placed in a refrigerator without previous pickling. The hides were salted and refrigerated at 6° C., placed in piles, and stored protected from air and sunlight. The 800 kg. of hides, when tanned into black boxcalf, were free from stains or punctures, and the grain was very nice. Experiments are in progress on preventive treatments on fresh hides which have been pickled. The hides are agitated to complete penetration in the following baths at 18° C.: mercuric bichloride (1.3 g/l), sodium cyanide (1.5 g/l), and sodium fluoride (2.0 g/l). The hides are then preserved with salt. Experiments done in 1957–58 revealed that in one case where the greatest precautions of cleanliness and care were taken, red spots appeared on skins after only one week. The piles of skins were flooded with sunlight and exposed to air currents. All parts of the flesh side exposed to air were red. In the interior of the pile no trace of coloration was visible. In other cases alterations such as red and violet stains occurred despite antiseptics and the best care when the piles were not absolutely protected against the ambient conditions. R.L.H.

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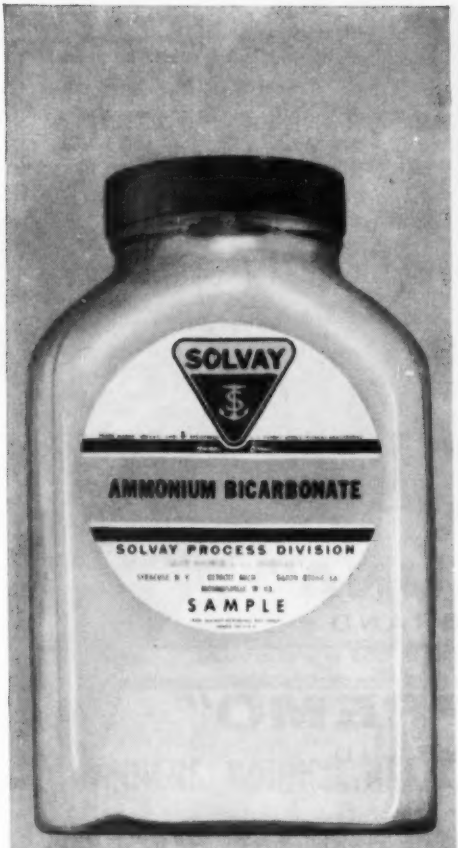

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New Esterified Oils Offer Major Benefits To White Tanners

An important development was announced recently by a leading manufacturer of tanning chemicals.

After considerable basic research, Seaboard Chemicals, Inc. is the first to offer the tanner a new concept in white leather fatliquors. It's a series of esterified oils called the Polarsols.

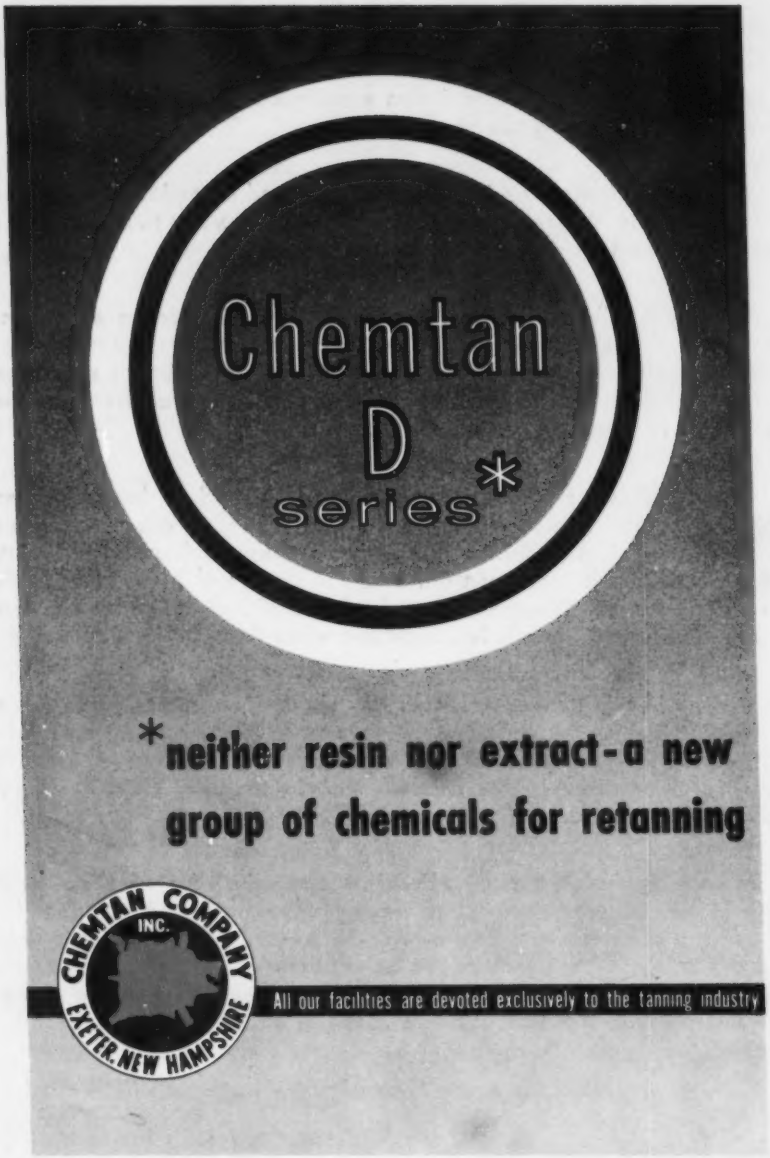
Tannery production runs indicate that these oils possess an attractive combination of properties that can help white tanners get more top-grade leather per pack and those already using the Polarsols claim the temper of their stock can be kept under absolute control, from mellow all the way to super-soft.

Unlike ordinary sulfated oils, which tend to produce looser leather as oil percentage increases, Seaboard's new esterified oils produce an overall tight break regardless of oil percentage used. Reports from the field indicate this is true even out into the flank and belly areas, with the result that an unexpected bonus of additional high-grade leather can be produced. And there is less trimming when the stock is finished.

To check oxidation characteristics, rigid Fadeometer tests have been conducted over a period of time on various types of leathers fatliquored with the Polarsols. These bleached esterified oils proved to be unusually light fast. Also the Polarsols showed excellent stability where residual alum was present.

Perhaps one of the most attractive characteristics of these new esterified oils is the amount of money they save. According to Seaboard, the Polarsols soften leather to a greater degree than sulfated oils, so significant savings can be expected. Field experience has borne this out, with many tanners reporting they can get the same degree of softness in their stock with 20% less oil.

There is a Polarsol for every type of white leather—whether it be sides or splits, suedes or grains, kid or calf. The manufacturer offers percentage suggestions for use. To get detailed information and a trial sample of one of the Polarsols, specify your type of leather. Write or phone Seaboard Chemicals, Inc., Dept. 11G, 30 Foster St., Salem, Massachusetts, U. S. A. In Canada: Tennant & Michaud, Ltd., Toronto and Montreal.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